A

M.TECH THESIS

ON

"OPTIMIZATION IN THE TREATMENT OF SPENT POT LINING - A HAZARDOUS WASTE MADE SAFE"

MASTER OF TECHNOLOGY

IN

Chemical Engineering

SUBMITTED BY

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CERTIFICATE

This is to certify that the Project report entitled, **"Optimization in the treatment of Spent Pot Lining - A Hazardous Waste Made Safe"** submitted by Pankaj D. Indurkar**,** Roll No. 212CH1074 for the award of the Master of Technology Degree in Chemical Engineering at National Institute of Technology, Rourkela is prepared by him under my supervision and guidance.

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Date:

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ABBREVIATIONS

SPL- Spent Pot Liner

ANOVA-Analysis of Variance

CHNS-Carbon, Hydrogen, Nitrogen, Sulfur

L/S Ratio- Liquid to Solid Ratio

RSM- Response Surface Methodology

SEM- Scanning Electron Microscope

EDX- Energy Dispersive X-ray

TGA- Thermo-Gravimetric Analysis

XRD- X-ray Diffraction

GCV- Gross Calorific Value

DSC- Differential scanning calorimetry

LIST OF SYMBOLS

x_1 - Acid concentration

x_2 - Alkali concentration

x_3 - L/S ratio

x_4 - Temperature

S- Response variable

R^2 - amount of variation in the observed response values

ABSTRACT

The increase in demand of aluminium leads to production of more Spent Pot Lining as well as more environmental problems. The objective of this study is to optimize the process parameters so as to get the maximum amount graphitic carbon by employing sodium hydroxide fallowed by percholoric acid and sodium hydroxide fallowed by sulfuric acid for the first time. Both “one factor at a time” and “taguchi method”, “Response Surface Methodology” approaches for optimization have been adopted to get the significant process parameters such as alkali concentration, acid concentration, L/S ratio and temperature. A feasibility study was also conducted in cryolite precipitation at two different pH. XRD, SEM-EDX, proximate and ultimate analysis were done on the SPL samples for mineralogical as well as elemental analysis. The carbon percentage of SPL has been increased from 42.19 to 87.03% as confirmed from the ultimate analysis. From the proximate analysis, the fixed carbon for perchloric acid treatment was found to be increase from 38.96% to 82.86 % from the raw to final treated SPL and for sulfuric acid treatment fixed carbon was found out to be increase from 38.96% to be 78.68%. From the calorific value determination it is seen that the heating value of raw SPL (2865.041 cal/g) has substantially increased to 6533.647 cal/g and 6689.694 cal/g respectively by using perchloric acid and sulfuric acid.

Key words: Spent pot liner, Taguchi method, Response Surface Methodology, Chemical leaching

CHAPTER 1

INTRODUCTION

1. INTRODUCTION

1.1 Some facts about Aluminium:

Aluminium is the third richest chemical element of the earth crust and generally it is combination of silicon and oxygen in rock forming silicate minerals. Production of aluminium in India started in 1938 with the commissioning of Aluminum Corporation of India (INDAL) plant in association with the Alcan with a capacity of 2,500 ton per year. It started with the production sheets by means of imported aluminum ingots. Hindustan Aluminum Corporation was put up in 1959 at Renukoot (UP) having an initial capacity of 20,000 ton per year. Madras Aluminum Corporation, a PSU was set up in 1965 with a capacity of 10,000 ton per year followed by Balco in 1975, a PSU with a capacity of 10,000 ton per year. Finally National Aluminum Company (NALCO), a PSU with a capacity of 0.218 mn tons was commissioned in 1987 with the collaboration of Pechinery (France). In 1970s, the government brought aluminum industry under control by price distribution controls and barriers to entry. In 1970 Aluminum Control Order forced the Indian enterprises to give 50 % of the produced aluminum for electrical purposes. Then in 1989, government release the industry with the withdrawal of the Aluminum Control Order with subsequent de-licensing the industry in 1991 and allowing the liberal import of capital goods and technologies. In 80s the aluminum demand grew at 6 %. A growth rate of 12% registered due to the Aluminum order post liberalization. This united with the increase in the aluminum prices worldwide ($1800/ ton in 1994) provide a route to increased investments of this sector. In aluminum industry the downstream capacity pumped because of adequate duty differential amongst aluminum ingots or primary metal and value added downstream products. In March 1993 whereas the duty on aluminum ingots was 25% the duty on downstream products was 70%. However in the 1997 budget the modification in the tariff structure was undertaken, semi-fabricated metal duty was reduced to 25%. This variation adversely influenced the fortunes of the downstream producers.

In 1821 ferruginous aluminous rock (27.6% Fe_2O_3, 52.0% $A1_2O_3$, 20.4% H_2O) investigated by the Berthier chemist (French). This rock found nearby the village of Les Baux in southern France. From chemical analysis he concluded that alumina occurred as a dihydrate mineral ($A1_2O_3.2H_2O$) a estimation since refuted. In 1844, Dufrenoy, a French scientist defined the Les Baux mineral as bauxite. The term bauxite now is applied normally to a rock that contains significant amounts of aluminum hydroxide minerals.

1.2 Spent Pot Lining (SPL):

SPL emerges throughout the manufacture of metallic aluminium following advanced industrial processes. SPL could be a contaminated graphite/ceramics cell lining waste created from the manufacture of primary aluminium. The most common aluminium ore, bauxite, is employed as a source of alumina. This alumina is the feedstock for the smelting operation, i.e. aluminium metal production, where alumina is dissolved with cryolite in large carbon or graphite lined steel electrolytic cells known as "pots". These pots operate constantly with an operating lifespan of normally 5-8 years.

1.3 Manufacture of Pure Alumina ($A1_2O_3$):

Bauxite became the main ore for aluminum fabrication when Hall and Héroult discovered an efficient process for extracting aluminum from pure alumina ($A1_2O_3$) in 1886. In 1887, Bayer established a method for producing pure alumina from bauxite.

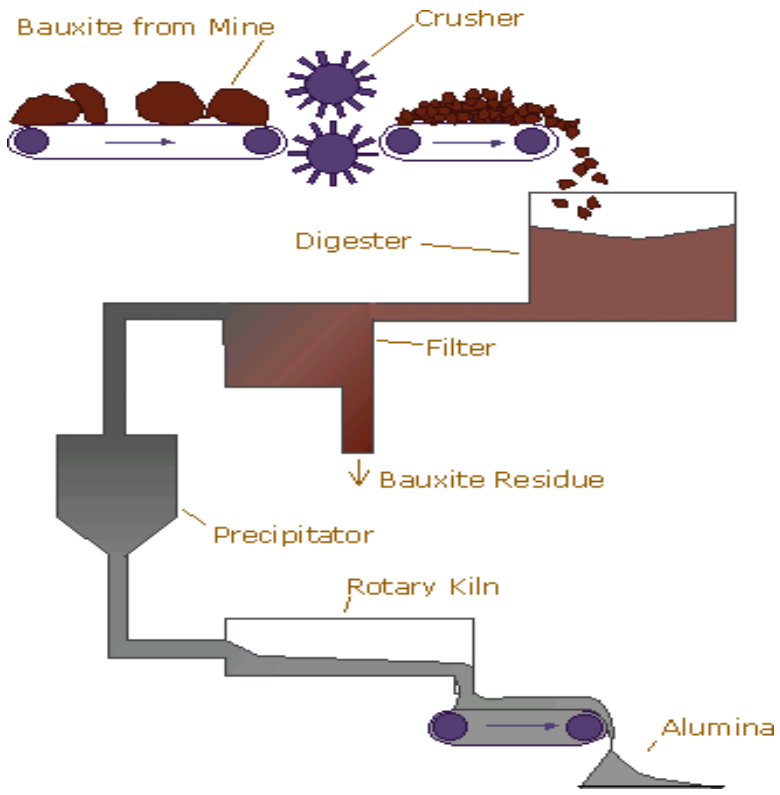


Figure 1.1: Flow sheet of the Bayer process

In the Bayer process, bauxite is processed by washing with a hot solution of caustic soda, NaOH, at 175 °C, under pressure. This alters the alumina within the ore to soluble sodium aluminate, $2NaAl(OH)_4$, according to the chemical equation 1.1.

$$Al_2O_3 + 2\ NaOH + 3\ H_2O \rightarrow 2\ NaAl(OH)_4 \qquad 1.1$$

This treatment aditionally dissolves silica, but the other components of bauxite don't dissolve. Occasionally lime is added here, to precipitate the silica such as calcium silicate. The solution is clarified by filtering off the solid impurities, usually through a rotary sand trap, and a flocculent for example starch, to become rid of the fine particles. The solid impurities mixture is called red mud. Originally, the alkaline solution was cooled and treated by effervescing carbon dioxide into it, through which aluminium hydroxide precipitates.

$$2\ NaAl(OH)_4 + CO_2 \rightarrow 2\ Al(OH)_3 + Na_2CO_3 + H_2O \qquad 1.2$$

But later, this provided way to seeding the supersaturated solution with high-purity aluminum hydroxide [$Al(OH)_3$] crystal, which removed the need for cooling the liquid and was more economically viable.

$$NaAl(OH)_4 \rightarrow Al(OH)_3 + NaOH \qquad 1.3$$

Then, at 980°C, the aluminium hydroxide decomposes to aluminium oxide, discharge of water vapor in the method.

$$2\ Al(OH)_3 \rightarrow Al_2O_3 + 3\ H_2O \qquad 1.4$$

Since alumina is produced from the ore bauxite by means of the Bayer process at an alumina refinery. The Bayer process, which continues to be the most inexpensive method, takes benefit of the reaction of aluminum tri-hydroxide and aluminum hydroxide oxide with aqueous sodium hydroxide to form sodium aluminate.

1.4 Electrolysis of Alumina

Aluminum is extracted from alumina by smelting process, generally by Hall-Héroult process.

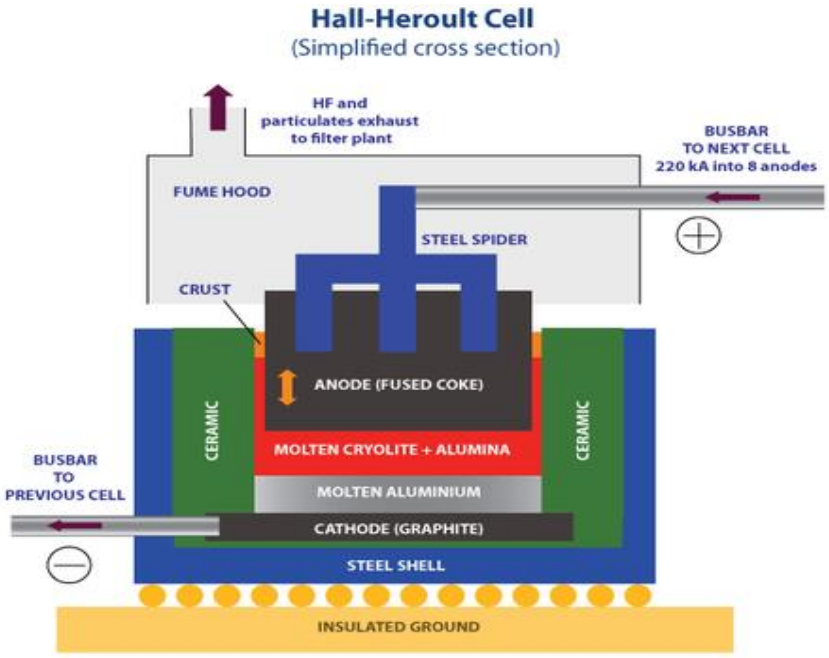


Figure 1.2: Hall-Heroult Cell With process Flow Diagram

Hall-Heroult process comprises reduction cell called a `pot' which is made up of steel rods, with a carbon cathode lining reinforced by refractory bricks inside a steel shell. Alumina (Al_2O_3) is dissolved in molten cryolite (Na_3AlF_6) and electrolyzed by passing voltage through it. Eventually the cell fails because of working failure or poor cell performance caused by the degradation of the carbon cathode lining or as the voltage increases or iron starts to be detected in the aluminum metal. When this happen the pot lining is removed and the shell is re-lined. The waste material, thus generated, is fabricated of refractory brick insulation, graphitic carbon and cell electrolyte toget her with the minor side products generated during cell operation such as sodium cyanide, aluminum carbide (Al_4C_3), aluminum nitride (AlN), aluminum metal, sodium metal. Leachable fluoride (up to 20 wt. %) and cyanides (up to 1 wt. %) are the main environmental concerns. SPL contains some valuable inorganic compounds, such as Na_3AlF_6, NaF, CaF_2, Al_2O_3 and $NaAl_{11}O_{17}$. The inorganic content in the SPL varies from 25% to 50% depending on the condition of cell. Besides the inorganic compounds, the other configuration in the SPL is carbon that has graphitized at high temperature of 800-900 °C for a number of years. Graphitized carbon and inorganic compounds in SPL are important resources.

Spent Pot liner (SPL) is a contaminated graphite/ceramics cell waste generated in the primary production of aluminum. In past SPL was dumped in rivers or in the sea, or stored it in open dumps or land filling. But these methods is not accepted because leachability of fluorides

and cyanides. As a result recently the SPL is stored in secured landfills where it is placed on an impermeable base made of clay and covered with a heavy plastic liner and an impermeable cap. Alternatively it is stored in sheds that have a concrete base. These storage arrangements are costly and there will be substantial increase in costs as more and more SPL is generated.

Since spent pot lining has been declared a hazardous waste by the U.S. Environmental Protection Agency in the year 1988, cause a typical challenge for many organizations in this industry and in many countries, SPL has been identified as an highly problematic hazardous waste because it comprises concentrations of cyanide and fluoride and gives off noxious and flammable gases once interaction with moisture. These contaminants readily "leach" into the surrounding soils and groundwater during both short term and long term storage and can cause potential contamination of drinking water reserves. Due to this concern, SPL should be managed and disposed of in an applicable manner.

1.5 Chemistry:

Although the mechanism of electrolysis is still poorly understood, most investigators approve that cryolite ionizes to produce hexafiuoroaluminate (AlF_6^{3-}), which dissociates to form tetrafluoroaluminate (AlF_4^-), sodium (Na^+), and fluoride (F^-) ions.

$$Na_3AlF_3 \rightarrow 3\ Na^+ + AlF_6^{3-} \qquad 1.5\ (a)$$

$$AlF_6^{3-} \rightleftharpoons AlF_4^- + 2\ F^- \qquad 1.5\ (b)$$

Aluminium oxide dissolves at low concentrations by forming oxyfluoride ions using a 2:1 ratio of aluminum to oxygen ($Al_2OF_{2n}^{4-2n}$); at higher $A1_20_3$ concentrations, oxyfluoride ions using a 1:1 ratio of aluminum to oxygen ($AlOF_n^{1-n}$) are produced.

$$Al_2O_3 + 4\ AlF_6^{3-} \rightarrow 3\ Al_2OF_6^{2-} \qquad 1.6\ (a)$$

$$Al_2O_3 + AlF_6^{3-} \rightarrow 3\ AlOF_2^- \qquad 1.6\ (b)$$

Electrolytic cells are usually operated with 2-6 wt. % alumina in the electrolyte. Saturation ranges between 7-12% alumina depending upon composition and temperature.

From the ion transport measurements it specifies that Na^+ ions carry most of the current; however, aluminum is deposited. Most likely a charge transfer take place at the cathode interface and hexafluoroaluminate ions are discharged, forming aluminum and fluoride ions to neutralize the charge of the current carrying Na^+ ions.

$$12\ Na^{+} + 4\ AlF_6^{3-} + 12\ e \rightarrow 12\ (Na^{+} + F^{-}) + 4\ Al + 12\ F^{-} \qquad 1.7$$

Oxyfluoride ions release on the anode, forming CO_2 and $A1F_6^{3-}$ ions.

$$6\ AlOF_2^{-} + 3\ C + 24\ F^{-} \rightarrow 3\ CO_2 + 6\ AlF_6^{3-} + 12\ F^{-} + 12\ e \qquad 1.8$$

On adding of anode and cathode equations 1.7 and 1.8, plus solution of alumina 1.8 offers the overall reaction.

$$2\ Al_2O_3 + 3\ C \rightarrow 4\ Al + 3\ CO_2 \qquad 1.9$$

1.6 Spent Pot Liner Waste Challenges:

SPL dumping and utilize is a universal challenge for primary aluminium industry. SPL is a mixed hazardous waste that consists of carbonaceous materials and refractories. It is removed from the cells when they are relined at the end of their operational lifespan. Throughout a pots operative life, numerous chemicals that are extremely toxic, corrosive and water reactive kind and/or accumulate within the cell lining.

The production primary aluminium in world was twenty three million tonnes in 2009 with continuous growth predicted in the medium term. Requirement of aluminium is increasing and this growth is presently expected to carry on for the predictable future. The SPL waste is heterogeneous owing to the variety of bauxite sources and variants of technological origin and so a strong and adaptable waste management solution is needed. The manufacture rate of SPL is around 22 kg per metric tonne of primary aluminium manufactured, so the projected world SPL market in 2009 was capable 515 ktpy. Unit treatment prices in 2009 generaly ranged from $400 - $1200 per metric tonne of SPL, this wide value range reflects economies of scale and also the effects of native conditions.

1.7 Objective of the project:

To utilize spent pot lining, a hazardous waste from aluminum industry as a fuel in power plant.

1.7.1 Specific objective:

- Enrich the carbon percentage of SPL sample using leaching process.
- Treatment of SPL with NaOH, $HClO_4$ and H_2SO_4.
- To get optimum process parameter using 'Taguchi Design', 'Response Surface Methodology' and 'Classical Approach of Optimization'.
- Characterization of samples.
- Fuel value analysis optimized samples obtained from leaching experiments.

CHAPTER 2

LITERATURE REVIEW

2. LITERATURE REVIEW

Besides certain 40m ton per year of primary aluminium, globally smelters produced about a million tons per year of spent pot lining which is a hazardous waste. This means around 25 kg of SPL generated per tonne aluminium production. Up to now, most of this SPL has departed to landfill. This would like modification if the industry wants to claim a sensible degree of sustainability and environmentally tolerable emissions. For processing of spent pot lining an excellent summary was conferred by Sørli and Øye [2]. Liu and Lou [4] initiate that the carbon hearth prepared from anthracite and/or graphite undergoes nice changes in its different chemical compositions, physical properties, internal microstructures, carbon morphology and crystalline structure throughout the aluminium smelting process. Usually, there are certain treating methods for SPL, together with hydrometallurgical and pyrometallurgical processing, for example physical separation, thermal treatment and chemical leaching procedures [5]. The difference in solubility, density and surface properties between carbon and fluorides play an important role in physical method to separate carbon and fluoride. For SPL treatment, the froth flotation technology is physical separation process [6]. The mostly applied physical, chemical, and thermal methods to process spent pot lining are ineffective, however they might be reduced or possibly eliminated, according to Young [7], if the pots were designed for recyclability by means of a management technology which has been explained. So, as recommended by Sturm et al. [8] thermal insulation of electrolysis pots uses aluminium oxide rather than refractory bricks. The study of Krüger [9] is tabulated in table 2.1.

Table 2.1 SPL typical components and concentration

Component	Both cuts together (100%)	1st cut carbonaceous (56%)	2nd cut refractory (44%)
Carbon	33.1	54-94	18.2
Total fluoride	15.7	6-20	4-10
Free alumina	22.3	0-15	10-50
Total aluminum	15.1	5-15	12.6
Calcium	1.8	0.5-4	1-6
Quartz	2.7	0-6	10-50
Phosphorous	0.3	0-650 g/t	0-300 g/t
sulphur	0.1	0.1	0.1

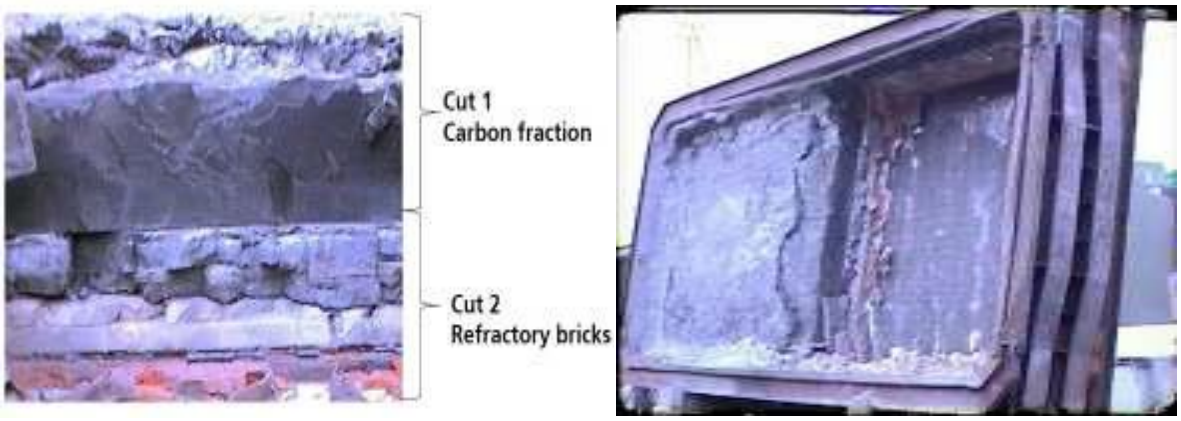


Figure 2.1 Spent pot linings

2.1 Thermal processes:

Crushing SPL on site and transferring it in bulker bags was projected [10]. Carbon percentage in SPL is high; so this can be used as a fuel such as in the brick, cement and pig iron industries. For crushing SPL, Chen and Li [12] proposed its physical behaviour. They had seen that graphite and sodium in SPL make it sticky, slippery and very problematic to crush. They also conceded tests to state the chemical stability of the fluorides within the SPL [12]. Crushed first cut SPL can be employed as collar paste for protecting anode stems [13].

In the USA disposal of SPL in land without inertisation is prohibited [24, 15]; it is termed as hazardous material because of its leachable fluorides and cyanides. Possible treatments comprise crushed SPL heating to about 1000 °C and to oxidize cyanides lime is added and to bind the fluoride, as suggested by Karpel [16] and by Li and Chen [17]. Oliveira et al.[18] suggested to heat 2nd cut SPL up to more than 750°C to take out molten and volatile impurities , while Utkov et al. [19] treat the carbon rich part with an $FeSO_4$ solution so as to neutralize water soluble NaCN. Courbariaux et al. [20] recommend treating crushed SPL in a circulating fluid bed. Balasubramanian et al. [21] suggested vitrification of SPL by small additions of glass former along with traces of nucleation agents to support crystallisation, and then melting at about 1300 °C.

Then Lazarinos [22, 23] treated the SPL in gasification combustion, the main purpose being to terminate cyanide compounds mostly present in the carbon fraction. Due to high energy and fluoride content, Blinov and coworkers [24] offered a pyrohydrolysis procedure to recover fluorine as HF, while the carbon rich portion is employed in the manufacturing of pig iron.

The progress of the Ausmelt process to treat SPL was studied several times [16, 25] during 2001 and 2004. In 1995 Portland Aluminium of Australia spent about US$16m to build a research and development processing facility for SPL treatment. Alcoa, in collaboration with Ausmelt Ltd., employed a pyrometallurgical process to combust and melt SPL. On other side this produces hydrogen fluoride laden gas, which is cooled and transformed into aluminium fluoride, and on the other side it produces inert sand.

2.2 Chemical processes:

A low-technical process is required to treat SPL material, but processing the cathode wastes (carbon cut and refractory cut) only with water [26] does not seem sufficient to remove all harmful elements. Therefore Baranovskii [27] put forward to crush first cut material, to blend it with limestone, and then to add this mixture to an aqueous slurry so as to recover soda and potash.

As aluminium electrolysis carbon froth and spent pot lining are inevitable, Lu et al. [28] offered to separate these constituents by flotation. In this respect Mirsaidov et al. [29] proposed to use kerosene and pine oil as flotation agents. On other hand the scientists separated a cryolite-alumina concentrate; they burnt out the remaining carbon at 800°C in a rotating furnace.

The principles for leaching SPL were explained by Silveira et al. [30, 31]. They had seen that for all the pots studied the pH of SPL is at 10-11.8, and total determined fluoride content at high pH was 5.13-11.41%. But the total fluoride content in leached liquid at pH 5 was only 0.26-3.46%. Therefore leach liquid must be alkaline above ph 12 in order to efficiently process SPL. Leaching SPL with water and concentrated H_2SO_4 was offered by Zhao [32] to recover HF. The liquids are filtered for the manufacture of graphite powder, aluminium hydrate and alumina, while fluorides and sulphates are produced from the filtrate. Lisboa et Steel [33] studied the leachability of NaF, CaF2 and cryolite from spent potlining. By manipulating solution equilibira, they precipitated fluoride in a form that can be recycled into the pot. Following removal of fluoride, they attained high degrees of separation of graphite from the remaining refractory compounds by using a density separation technique. Platt [34] put forward the complete treatment of spent pot lining and salt slag in order to avoid landfill. Electrolysis produces 22-24 kg/t of spent pot lining per tonne of aluminium. Spent pot lining is hazardous due to its high cyanide and fluoride contents. Befasa collects such a material together with salt dross from remelters to treat chemically at special sites. Besides gases such as hydrogen, ammonia,

methane, etc., at the end of the reaction stage Befasa gets solids which are pumped to a vacuum belt filter. Here the resulting oxides and solids undergo in-process testing to confirm reduced levels of water-soluble chlorides in line with customer requirements.

Alcan identified its low caustic leaching and liming (LCL & L) hydrometallurgical method as the most efficient means of recuperating the chemical values contained in SPL. This method Alcan has reviewed several times [35, 36].

2.3 Rio Tinto Alcan—LCL&L Process:

In 2008, RTA built an 80 kilo ton per year (ktpy) SPL treatment plant in Jonquiere (Que´bec) based on the low-caustic leaching and liming process (LCL&L) [37,38] developed at the Arvida Research and Development Center (ARDC; Jonquiere, Quebec) in the early 1990s. Figure 2.2 shows a simplified flowsheet of the process that was implemented at RTA's SPL treatment plant.

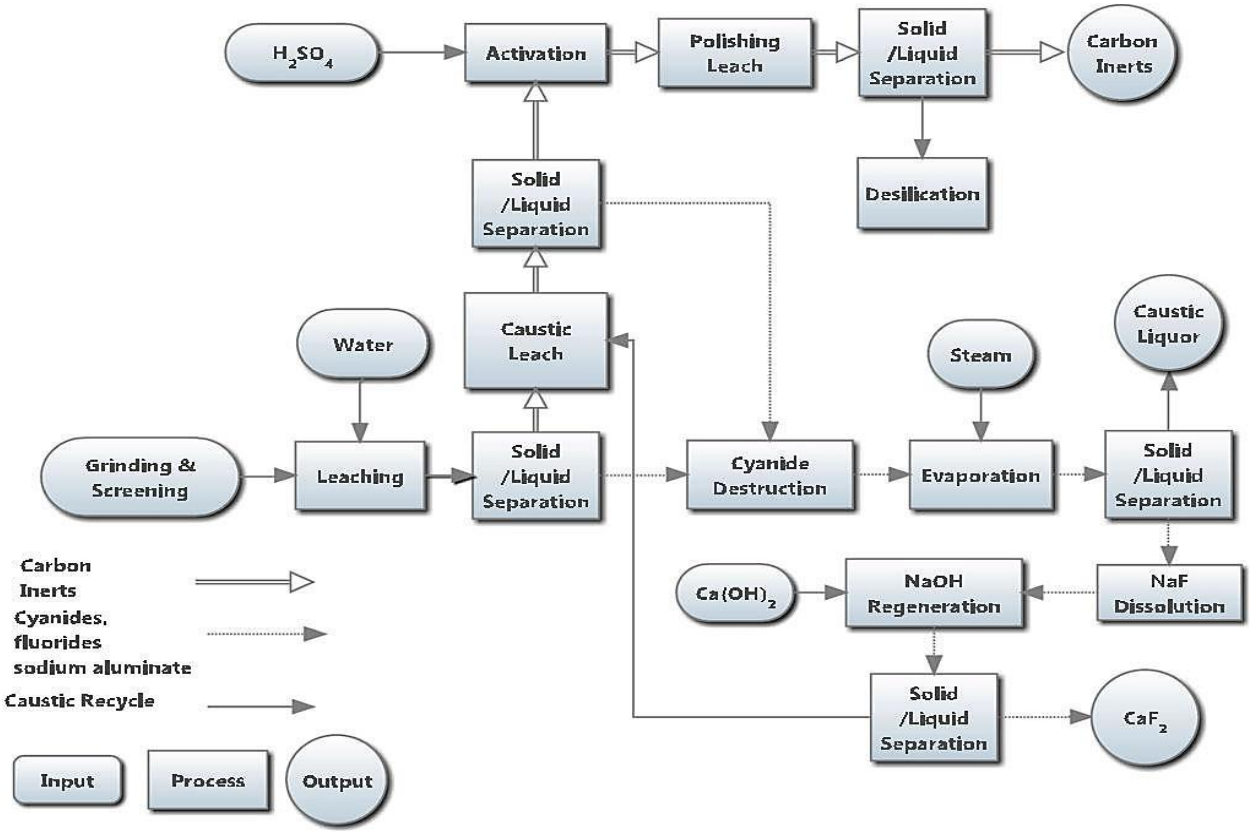


Figure 2.2 Rio Tinto Alcan—LCL&L simplified flow sheet.

On this flow sheet of the LCL&L process, a first water leach was done to minimize the quantity of liquor that had to be brought at high temperature because a very small amount of

cyanides is soluble under those conditions. As seen in Figure 2.2, by evaporating the low-caustic liquor comprising the dissolved sodium fluoride, it precipitates out of the solution when the NaOH concentration is brought to 250 g/L. At that concentration, the fluoride level turns out to be very low and the concentrated liquor can be used directly in the bayer process. For the reason that the market for the NaF is limited, sodium fluoride is converted to calcium fluoride and is caustic by reacting NaF with lime. By doing so, calcium fluoride (fluorspar) can be used for the manufacture of aluminum fluoride for electrolysis, closing the loop for the fluorides. Finally after a caustic leach, the sodium ion concentration in the carbon-brick fraction is reduced considerably and the fluorides and cyanides are removed, thus making the residual solids an acceptable feed for cement. However, an important drawback is its reduced calorific value due to the existence of water. Also, because of its nontoxicity, landfilling could provide a fallback situation in case of a failure with the valorization routes. For this to become possible, the carbon brick fraction must have the leachable fluorides lower the 150 ppm maximum limit in Quebec and a pH below 12.5. This was attained with the H_2SO_4 activation and polishing leach. In addition, once the plant is up and running, the research program on the development of the valorization of the carbon-brick fraction beneficiates. The carbon-brick fraction can be separated by flotation and could produce a high-value carbon; the brick can be used in cement kiln. The separation by flotation is at pre engineering. Meanwhile, the material is stored. In 2012, some 60700 tons of SPL were handled at RTA's SPL treatment plant. However, even if the plant ramp-up follows a steep curve, some challenges keep on to be overcome in particular to reach the initial goal of a total recycling of SPL.

2.4 Alternate Processes to Primary Aluminium Smelting (Emerging Technologies):

There are a number of research initiatives presently underway to manufacture primary aluminium while concurrently reducing energy consumption and emissions. These contains

- *Inert Anodes:* Carbon-free anodes that are inert, dimensionally stable, that are slowly consumed, produce oxygen instead of CO_2. The use of inert anodes eliminates the necessity for an anode carbon plant (and PAH emissions from the process).
- *Wettable Cathodes:* New cathode materials or coatings for existing cathode materials that gives higher energy potency.
- *Vertical Electrodes – Low Temperature Electrolysis ("VELTE"):* The method uses a non-consumable metal alloy anode, a wetted cathode and an electrolytic bathtub,

that is unbroken saturated with aluminium oxide at the comparatively cold of 750°C by means that of free aluminium oxide particles suspended within the bathtub. This technology might turn out primary aluminium metal with lower energy consumption, lower cost, and lower environmental degradation than the standard Hall-Héroult method.

- *Drained Cell Technology:* Features the coating of aluminum cell cathodes with titanium dibromide and removing the metal pad, that reduse the gap between anode and cathode, thereby lowering the desired cell voltage and reducing heat loss.
- *Carbothermic Technology:* Carbothermic reduction produces aluminum employing a chemical reaction that takes place inside a reactor and needs much less physical space than with the Hall-Héroult reaction. This method would result in considerably reduced electrical consumption, and also the elimination of perfluorocarbon emissions ensuring from carbon anode effects, hazardous spent pot liners, and hydrocarbon emissions related to the baking of expendable carbon anodes.
- *Kaolinite Reduction Technology:* The manufacture of aluminum by reduction of aluminum chloride using clays holds appeal because the raw materials are readily available and inexpensive. The thermodynamics also provide high-speed conversion reactions with lower electrical demand and no bauxite residue is created.

2.5 Industrial uses of SPL:

The literature tells that untreated spent pot lining can be used especially in the cement industry and also in pig iron or steel making. For first and/or second cut SPL other notable solutions have been developed.

2.5.1 Cement kiln

Processing SPL in klinker furnaces has been projected several times [39, 40]. Generally the first cut serves as fuel whereas the second cut of SPL serves as klinker aid [41, 42]. Venancio et al. [43] determined the calorific power in the 1st cut of SPL to be up to 5 MJ/kg. Therefore the coke fuel for the klinker chamber could be reduced by 111 tpm, and also the klinker forms at a lower temperature by 80°C allowed the employment of a less expensive coke with higher sulphur content, with no impact on emissions.

Hillside and Bayside Aluminum have worked for years with Pretoria Portland Cement to develop a one-step solution. Introducing SPL into the cement oven at warm temperature destroys cyanides and binds fluorides with calcium which is present in the cement or lime.

The carbon rich 1st cut of SPL is, in line with Cardoso [44], a high calorific material with a heat input of 16 MJ/kg, and also the 2nd cut is employed in huge quantities in the cement industry.

For Chen [45] it is only inert SPL, which might be recycled and forwarded as raw material for the manufacturing of cement.

2.5.2 Pig iron and steel

The use of SPL within the pig iron industry both as fuel and for decreasing the slag viscosity was described several times [46, 47]. SPL is added in amounts of between 5-25 kg/t pig iron [48] and also the SPL refractory part and bath material dissolves within the slag. Olsen [49] points out that the slag is designed so that any leaching of environmentally dangerous substance is minimized.

Rusal signed a cooperation agreement with the administration of the Kemerovo Region on usage waste to innovative products for ferrous metallurgy. During a beginning the Novokuznetsk Aluminum Smelter can offer up to 3,000 tpy of SPL to the environmental regional centre for processing.

For the making of special steels von Krüger [9] suggests to employ only the carbon-rich 1st cut SPL material. Volynkina and coworkers [50] see the chance to use 1st cut material as a additive for fuel.

2.5.3 Mineral Wool

Normally, rock wool is made from coke and blast furnace slag, and glass wool is made from sand and coke. Although trials have been conducted in France and Norway, first-cut SPL has only been used as an additive or substitute for coke in the mineral wool industry in Germany. It is limited to small quantities. Recently, Nørsk Hydro signed an annual contract with the mineral wool industry in Germany to accept untreated SPL. In France, one smelter's first-cut SPL was sent to the German mineral wool industry and the second cut was sent to a cement kiln.

2.5.4 Co-Processing SPL with Salt Slags

In Europe, dross is treated with salt to recover aluminum. The salt containing MgO and Mg_3N_2 and Al and other oxides residues has also be landfilled or the salt plus residues recovered by a hydrometallurgical process. BEFESA operates plants to recycle dross salt plus residues from dross recycling in Europe. BEFESA have found a synergy in that three parts salt plus residues added to one part ground and screened SPL reduces the energy input to operate their water leach process between 95 ^{0}C and 105 ^{0}C. The slurry from the reactor is divided in a soluble

component NaCl/NaF, which is added to the salt for dross treatment. The insoluble component is suitable for the cement or mineral wool industry.

2.5.5 Ferro Alloys

The use of SPL as an additive for ferroalloy production was also investigated ferrochrome (Russia and Kazakhstan) and ferromanganese (Brazil).

2.5.6 Special products of 2nd cut

Istomin [51] performed a full literature review on the utilization and use of fluorine containing wastes from the aluminum industry, and located out that the refractory rich 2nd cut of SPL can be employed in the fabrication of aluminum silicon alloys. Moxnes et al. [52] conjointly used 2nd cut material and tried this within the manufacturing of Al-Si alloys directly within the electrolysis pots. Crushed refractory rich SPL is mixed with aluminium oxide but does not exceed about 15 wt % that of normal industrial smelter grade aluminium oxide. This suggests that large and concentrated batches should be avoided.

Using 2nd cut material in foam-silicate manufacture was suggested by Proshkin et al [53]. This can be used as thermal insulation filling powder and as raw material for the manufacture of non-formed thermal insulating things and the Alouette Aluminum plant in Canada uses refractory material of spent pot lining for the manufacture of special movable concrete blocks, used for bordering highways, but also used as removable walls for rapid access to buildings' basements.

CHAPTER 3

MATERIALS AND METHODS

3. MATERIALS AND METHODS

3.1 Materials:

3.1.1 Instruments and its purpose

Table 3.1 Instrument and its purpose

Instrument	Make	Function	Operation conditions
Analytical balance	Sartorius (BS223S)	Weight measurement	1mg - 100g
pH meter	Systronics (361)	Measurement of pH	pH 1 to 12
Incubator shaker	Environmental orbital Shaker	Shaking of conical flasks used in leaching study	• Speed: 120 rpm. • Temperature: 25°C, 50 °C.
Scanning Electron Microscope-Energy-dispersive X-ray spectroscopy	JEOL (JSM-6480 LV)	To study the clear morphology about the structure and extent of leaching capacity of SPL samples. And the elemental analysis of samples.	• Magnification: up to 10000X • Resolution : 1µm • Detector: Everhardt Thornley secondary electron detector and Solid state backscattered detector. • X-Ray Analysis: Oxford Instruments ISIS 310 system with "windowless" detector. • Light element analysis: silicon detector with ATW.
Micro Centrifuge	Remi (RM12C)	Separation of precipitates from the leachate broth	• 8000 RPM for 10 min
CHNS analyzer	ELEMENTAR VARIO EL CUBE CHNSO.	Ultimate analysis- ASTM-D-3176	• Measurement of carbon, hydrogen, nitrogen and Sulphur of the SPL sample • Initial wt.- under 10mg
X-RAY DIFFRACTION ANALYSIS	Philips X'Pert X-ray diffractometer	Mineralogical and phase analysis of SPL samples.	• Cu Kα radiation generated at 35 KV and 30 MA • Scattering angle 2θ was ranged from 5° to 80° • scanning rate of 3 degrees/minute

TGA-DSC	TASDTQ600	Behavior of material under temperature increase,	• up to 800 °C (heating rate 10°C /min) under N_2 flow (100 ml/min) • up to 800 °C (heating rate 10°C /min) under O_2 flow (100 ml/min)
PSA-DLS	MALVERN MASTERSIZER HYDRO (2000MU	For particle size analysis by dynamic light scattering	• Measuring the random changes in the intensity of light scattered from a suspension or solution.
Hot Air Oven	WEIBER	For drying of samples	• Done at 110°C for 4 hours maximum
Magnetic Stirrer	SPINOT-TARSON, SPECTRO	For Stirring at high temperatures	• Speed: 120 rpm • Temperature: 75°C, 100 °C.
OVEN AND FURNACE	WEIBER, ADCO-ELECTRIC FURNACE	For proximate analysis: ASTM-D-3172,3173,3174,3175	• As per standards

3.1.2 Chemicals used:

Sodium-hydroxide (NaOH)

Perchloric acid ($HClO_4$)

Sulfuric acid (H_2SO_4)

3.2 Methods:

3.2.1 Collection of sample:

All the chemicals used in this investigation were analytical reagent grade of highest purity and obtained from Merck (Germany). The first cut SPL sample was being collected from Vedanta aluminium Ltd., Jharsuguda, Odisha (India). The SPL obtained from aluminium reduction cell was dried at 110°C for 2 hours and then crushed in Los Angeles Abrasion Machine then sieved to recover size fractions that can pass through the 52 BSS sieve or 300 micron sizes.

3.2.2 Experimental design:

3.2.2.1 Definition of Experiment design:

In an experiment, we deliberately change one or more process variables (or Factors) in order to observe the effect of the changes that will have on one or more response variables. The (statistical) design of experiments (DOE) is an efficient procedure for planning experiments so that the data obtained can be analyzed to yield valid and objective conclusions. Practical experiments are performed to prove theories and hypothesis, like wise in this work we are designing, analyzing our data systematically. very considerably conducting experiment brining out parameters or factors which influencing degree more ,process previously conducting experiments were very time consuming ,tedious jobs, also we can develop mathematical model to improvement of process. In statistical analysis experimental inputs knowingly changes to study output response of process.

3.2.2.2 Objective of experimental designing:

- To evaluate those variables which have most influential effect on Response.
- To get empirical model depending on independent variables so that response is almost desired value maximization or minimization.
- To minimize uncontrolled variables on output response.
- To find optimal process parameters.

3.2.3 Conventional approach of optimization:

For the conventional or "one factor at a time" approach of optimization, the effect studies were done at various process conditions. In the classical approach of optimization, the alkali concentration was optimized initially at various alkali concentration ranges from 0.5 to 3.5 mol/L. Then on the optimized alkali concentration, the effect of acid concentration (2.5 -10 mol/L) was done followed by effect of L/S ratio (1.5-4.5 cm^3/g) and temperature (25-100 °C).

3.2.4 Design of experiments by Taguchi method for optimization:

All the experiments were conducted at various concentrations of alkali and acid, liquid to solid ratio L/S and at various temperatures. This was done with "Taguchi 4 factors 4 levels design method" under the 120 rpm speed. The factors and levels are given in table 3.

Table 3.2 Taguchi 4 factors 4 levels

Sl. no.	Factors	Level
1	Alkali concentration (mol/L)	0.5, 1.5, 2.5, 3.5
2	Acid concentration (mol/L)	2.5, 5, 7.5, 10
3	Temperature (^{0}C)	25, 50 , 75 , 100
4	L/S ratio (cm^3/g)	1.5, 2.5, 3.5, 4.5

This method is applied for various types of physical and chemical process. Taguchi design approach helps in finding the effect of the factors on characteristic properties and the optimal condition of the factors. This is one of the better and simple ways to optimize design for performance, cost and quality. The advantage of the Taguchi optimization design over the conventional optimization is the experimental conditions are determined with least variability where as in conventional optimization it is determined on the basis of measured values of the characteristics properties. The Signal/noise ratio is used to measure the quality characteristics deviating from the desired value in Taguchi method. The experimental conditions having the maximum S/N ratio are considered as the optimal conditions, and the variability characteristics are inversely proportional to the S/N ratio.

3.2.4 Design of experiment by Response Surface Methodology:

A four factor and two level full factorial central composite design having alpha value 1 was used to determine the optimal factors of leaching percentage for the chemical treatment of Spent Pot Lining. Four independent variable namely acid concentration, alkali concentration, L/S ratio and temperature are taken in account for the calculation of leaching percentage. A total 31 different sets of combinations including 16 cube points (2^n , n= number of factors) for the calculations of linear terms 7 center point(n_c) in cube of the calculation of interaction terms and 8 axial point (2n) for the calculation of quadratic terms. The ranges of experimental parameters are given in the table 4.

Table 3.3 Ranges of experimental parameters

Sl. no.	Independent variables	Lower value	Higher value
1.	Alkali Concentration (mol/L)	1.5	3.5
2.	Acid Concentration (mol/L)	5	10
3.	L/S ratio (cm^3/g)	1.5	4.5
4.	Temperature (°C)	25	100

3.2.5 Leaching experiments:

The SPL leaching consisting of various steps: 50 g of sieved SPL having 300 micron size was washed with 250 ml of de-ionized water at 30°C for a period of 4 h. The reason for taking 5 liquid to solid ratio of the water washed treatment to get useful leachable fluoride value with a good concentration and the pH was around 11.56. After that's complete water washing was done to get all the leachate from the raw SPL. The XRD analysis was done on water washed SPL samples and showed that the water soluble NaF and Na_2CO_3 fractions had been removed which has been well confirmed by Lisbona [10, 16 and 17]. The sodium fluoride and sodium carbonate solution was filtered out using a MACHEREY-NAGEL MN 640 filter paper and the SPL residue was dried in an oven for the period of 4 hours at 110^0 C. The fractions of leachable fluoride in the form NaF and Na_2CO_3 are filtered out by the water washing of SPL. Leaching percentage was calculated by the following formula:

$$\%Leached = [L_0 - L_e]/(L_0) \times 100 \quad (3)$$

L_0, Le is the initial and final weight of SPL before and after leaching process in grams.

3.2.5.1 Cryolite precipitation:

Filtrates from leaching experiments on SPL acidic and alkaline treatment were combined at 75 °C and pH values at 4.5 and 9.5. The solution pH was maintained using water washed filtrate solution which is obtained from the initial water treatment of SPL i.e. at a 5 L/S ratio and having a solution pH around 11.56. The precipitates obtained was recovered by centrifugation at 3000 RPM, washed with de-ionized water to take off un-reacted ionic species and dried at 110 °C for a period of 4 h. Then the obtained samples were analyzed by XRD studies.

3.3 Characterization of spent pot liner:

3.3.1 Thermo gravimetric Analysis (TGA) / DSC:

Thermo gravimetric Analysis is a technique in which the mass of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere.

A TGA consists of a sample pan that is supported by a precision balance. That pan resides in a furnace and is heated or cooled during the experiment. The mass of the sample is monitored during the experiment. A sample purge gas controls the sample environment. The oxygen gas and nitrogen gas is flows that flows over the sample and exits through an exhaust in different set of analysis.

3.3.2 XRD analysis:

The powder X-ray diffraction (XRD) for the purpose of mineralogical analysis of raw SPL and treated SPL were determined by using Philips X'Pert X-ray diffractometer with a Cu Kα radiation generated at 35 KV and 30 MA. Scattering angle 2θ was ranged from 5° to 80° at a scanning rate of 3 degrees/minute and was analyzed using standard software provided with the instrument.

3.3.3 Ultimate and Proximate analysis:

The ultimate analysis was done for the purpose of determining the elemental compositions by using a CHNS analyzer; model ELEMENTAR VARIO EL CUBE CHNSO. For secondary composition purpose, proximate analyses of SPL samples were done according to the standard prescribed for coal and coke sample. For this ASTM standard of D-3172 (proximate), D-3173 (moisture), D-3174 (Ash content) and D-3175 (volatile matter) were adopted. For another set of experiment loss on ignition was done at 800 °C for 5 h [21] for the calculation of residue or ash content.

3.3.3.1 Moisture Content

$$A = 100\ X\ \frac{(F-G)}{(B-G)} \qquad (4)$$

Where G=Mass of empty crucible,

B= mass of crucible plus sample,

F= mass of crucible plus ashes sample,

3.3.3.2 Volatile Matter

$$V = 100 \text{ x } \frac{100X(B-F)-M*(B-G)}{(B-G)X(100-M)} \quad (5)$$

Where, B= mass of crucible with lid plus sample,

G=Mass of empty crucible

F= mass of crucible with lid plus ashes sample

3.3.3.3 Fixed Carbon Content

Fixed Carbon content is calculated by

% Carbon = 100 − (% Volatile matter + % Moisture content + % Ash content)

3.3.4 SEM-EDX analysis:

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image.

3.3.5 Calorific value analysis:

The calorific value (heat of combustion) of a sample may be broadly defined as the number of heat units liberated by a unit mass of a sample when burned with oxygen in an enclosure of constant volume. In this reaction the sample and the oxygen are initially at the same temperature and the products of combustion are cooled to within a few degrees of the initial temperature; also the water vapor formed by the combustion is condensed to the liquid state.

Thus the term calorific value (heat of combustion) as measured in a bomb calorimeter denotes the heat liberated by the combustion of all carbon and hydrogen with oxygen to form carbon dioxide and water.

CHAPTER 4

RESULTS AND DISCUSSION

4. RESULTS AND DISCUSSION

PART 1:

4.1 Taguchi optimization of Sodium hydroxide fallowed by Perchoric acid:

The main objective for the optimization is to know the effect of acid concentration, alkali concentration, temperature, L/S on the leaching percentage in rank wise.

4.1.1 Treatment of sample:

Raw sample collected from industry is passed through leaching process to purifying or remove the impurities. Leaching of the SPL sample was conducted at varying solid to liquid ratios (L/S) individually using alkali followed by acid.

4.1.2 Alkali leaching:

From the XRD analysis we obtained the peaks of inorganic compounds along with carbon. For purifying carbon, NaOH leaching was carried out on water washed SPL to separate carbon from inorganic compounds. In the second stage of experiment the water wash sample was taken for the alkali leaching. NaOH solution was used for the alkali leaching. The NaOH leaching experiments are carried out at concentration i.e. 0.5, 1.5, 2.5, 3.5 mol/L. The water wash SPL is taken at 120 rpm, at a various L/S ratios i.e. 1.5 2.5 3.5 4.5 and at various temperature range i.e. 25, 50, 75, 100 for 4 hr. After that water washing was done to remove the impurities and the pH of solid sample was decrease to neutral pH range this was done just to increase the leaching percentage and the optimum leaching percentage is found out accordingly. The reaction 4.1 and 4.2 is carried out to separate carbon from the inorganic compounds. Besides reactions (4.1) and (4.2), $Al(OH)_6^{3-}$, $Al_2(OH)_{10}^{4-}$ could be formed by reactions (4.3) and (4.4).

$$Na_3AlF_6 + 4\ NaOH \rightarrow NaAl(OH)_4 + 6\ NaF \qquad (4.1)$$

$$Al_2O_3 + 2\ NaOH + 3\ H_2O \rightarrow 2\ NaAl(OH)_4 \qquad (4.2)$$

$$Al(OH)_4^- + 2OH^- \rightarrow Al(OH)_6^{3-} \qquad (4.3)$$

$$2\ Al(OH)_4^- + 2OH^- \rightarrow Al_2(OH)_{10}^{4-} \qquad (4.4)$$

4.1.3 Acid leaching:

The sample obtained from the alkali leaching is then used for the next stage of acid leaching. The $HClO_4$ acid leaching experiments are carried out at different concentration i.e. 2.5, 5.0, 7.5, 10 mol/L. The SPL sample obtained after alkali leaching is taken at 120 rpm, at a

various L/S ratios 1.5 2.5 3.5 4.5 and at various temperature range 25, 50, 75, 100 ^{0}C for 4 h. After that water washing is done to remove the impurities and the pH of solid sample was decrease to neutral pH range this is done just to increase the leaching percentage and removal of other leachable impurities which are still in the solid samples. The optimum leaching percentage is found out accordingly.

Table 4.1 shows the experimental results for leaching percentage of water washed SPL with that of $HClO_4$ at different setting parameters with corresponding to S/N ratio.

Table 4.1 Taguchi design of NaOH fallowed by $HClO_4$

Sl. no.-	Alkali concentration (mol/L)	Acid concentration (mol/L)	L/S ratio (cm^3/g)	Temperature (°C)	Actual Leaching percentage (%)	Actual SN ratio	Predicted leaching percentage (%)	Predicted SN ratio
1	0.5	2.5	1.5	25	29.15	29.2928	29.2931	29.4162
2	0.5	5.0	2.5	50	39.67	31.9692	39.1331	31.8352
3	0.5	7.5	3.5	75	40.30	32.1061	40.7056	32.1417
4	0.5	10.0	4.5	100	50.45	34.0572	50.4381	34.0323
5	1.5	2.5	2.5	75	39.55	31.9429	39.5381	31.9180
6	1.5	5.0	1.5	100	45.12	33.0874	45.5256	33.1230
7	1.5	7.5	4.5	25	35.85	31.0898	35.3131	30.9557
8	1.5	10.0	3.5	50	42.79	32.6268	42.9331	32.7502
9	2.5	2.5	3.5	100	47.71	33.5722	47.1731	33.4381
10	2.5	5.0	4.5	75	44.12	32.8927	44.2631	33.0161
11	2.5	7.5	1.5	50	41.13	32.2832	41.1181	32.2582
12	2.5	10.0	2.5	25	36.10	31.1501	36.5056	31.1858
13	3.5	2.5	4.5	50	44.73	33.0120	45.1356	33.0476
14	3.5	5.0	3.5	25	36.79	31.3146	36.7781	31.2896
15	3.5	7.5	2.5	100	51.24	34.1922	51.3831	34.3156
16	3.5	10.0	1.5	75	46.79	33.4031	46.2531	33.2690

4.1.4 Analysis of the S/N ratio:

The word “signal” represents the desirable value(mean) for the output characteristics, and the word “noise” signifies the undesirable value[standard deviation(SD)] for the output characteristics in Taguchi method. Thus the S/N ratio is the ratio of the mean to the SD. Taguchi method uses the S/N ratio to measure the quality characteristic deviating from the desired value. The “nominal is best”, “larger is better” and “smaller is better” are there categories of quality characteristics in Taguchi method. Here “larger is better” is selected for the optimum leaching percentage calculation. The S/N ratio Y is determined by means of following equation,

$$Y = -10log\sum_{k=1}^{n}\binom{n}{k}x\mathrm{k}^{-2} \qquad \text{(a)}$$

Where n is the number of test and x_k are the comparison variables in the kth experiment.

Table 4.2 Response Table for Signal to Noise Ratios

Level	Alkali concentration	Acid concentration	L/S ratio	Temperature
1	31.86	31.95	32.02	30.86
2	32.19	32.46	32.31	32.47
3	32.47	32.42	32.55	32.59
4	33.13	32.81	32.76	33.73
Delta	1.27	0.85	0.75	2.87
Rank	2	3	4	1

Table 4.1 shows the experimental results for leaching percentage of water washed SPL with that of $HClO_4$ at different setting parameters with corresponding to S/N ratio. Orthogonal design layout is being adopted which helps in separating the parameter at different levels. For example, the means S/N ratio for acid concentration at levels 1,2,3 and 4 can be calculated by averaging the S/N ratios for the experiments 1-4, 5-8, 9-12 and 13- 16, respectively. In similar manner the means of S/N ratio for each level can be computed for other parameters. Figure 4.1 shows the S/N response graph. From the equation it is well understood that greater the value of S/N ratio then smaller is the variance of leaching percentage around the desired (larger is better)

value. However, the relative importance among of the process parameters for leaching percentage calculation still need to be known so that optimal combination of the process parameter levels can be determined more accurately. It is well elaborated in the following section. From the contour plot of we get the best operation conditions. The contour lines are calculated by distance method and the responses are shown in the fig. 4.2 and fig.4.3.

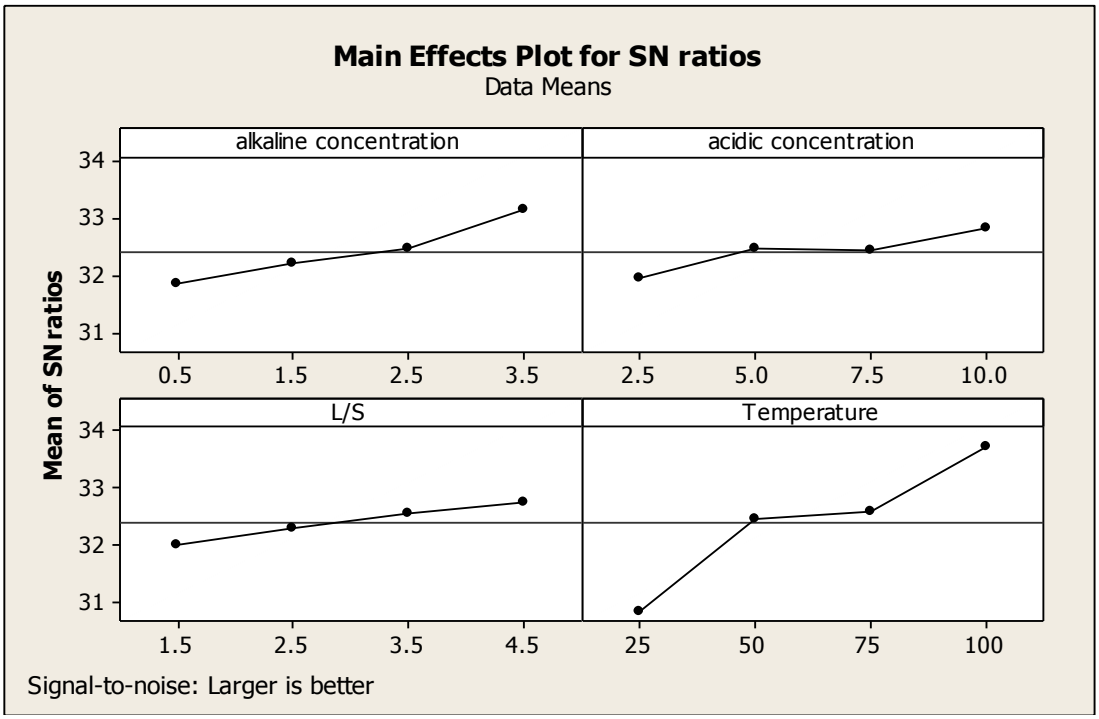


Figure 4.1 Main effect plot for SN ratios

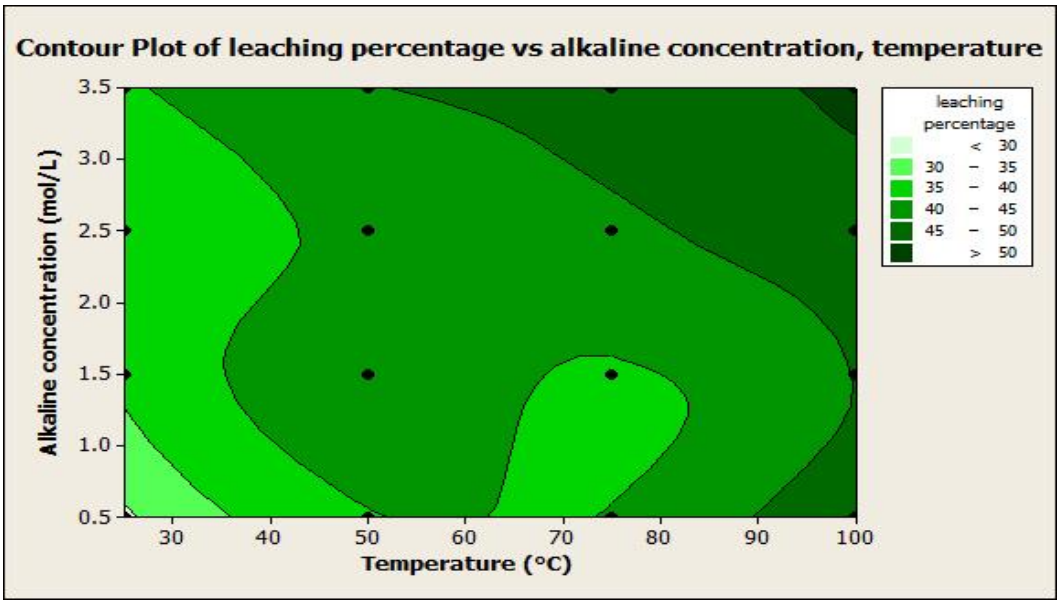


Figure 4.2 Contour plot of leaching percentage vs. alkali cocentration, temperature

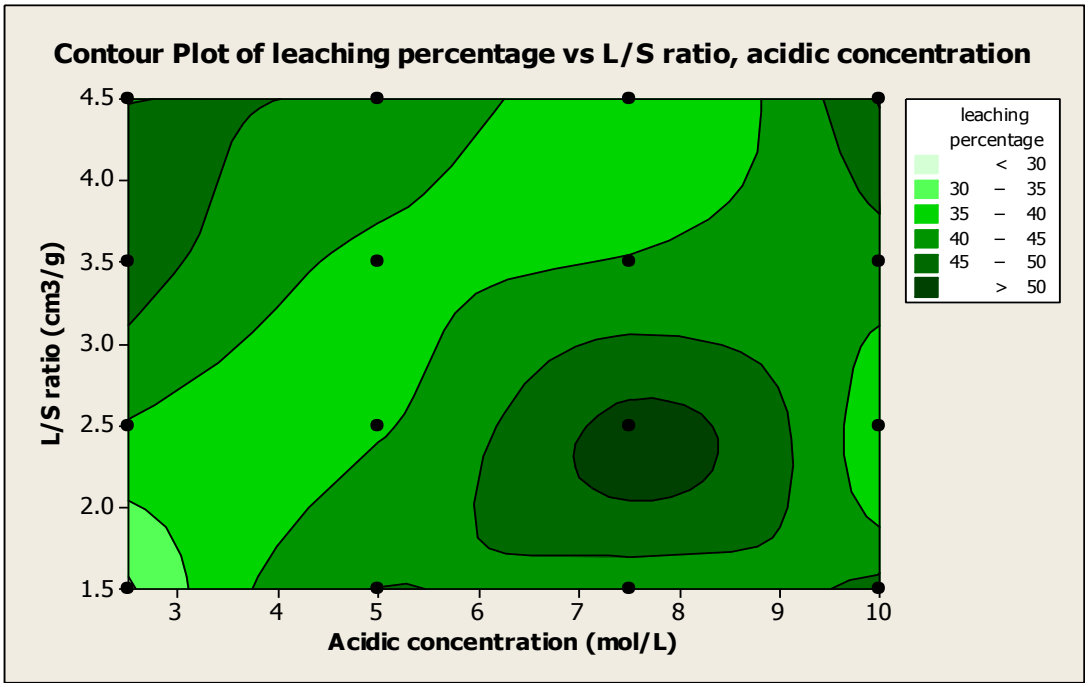


Figure 4.3 Contour plot of leaching percentage vs. L/S ratio, alkali concentration

4.1.5 Analysis of variance:

The reason of performing the analysis of variance (ANOVA) is to investigate which design parameters significantly affect the quality characteristics. F test has been conducted to know the significant effect on the quality characteristic. The F value is the ratio of the mean of the squared deviations of the mean of squared errors. Generally, when F>4 indicates that the design parameter has a significant effect on the quality characteristics. Table 4.3 shows the results of ANOVA for leaching percentage at various process and reaction conditions. Once the optimal level of the design parameters has been selected, the final step is to predict and verify the improvement of the quality characteristics using the optimal level of the design parameters.

The estimated S/N ratio using the optimal parameters for leaching percentage can be obtained, and the corresponding other parameters can be calculated by the equation (a). Table 4.1 shows the comparison of the predicted leaching percentage and the actual leaching percentage and the actual S/N ratio with that of Taguchi predicted S/N ratio. Results indicated that there is good agreement between the predicted and actual leaching percentage.

Table 4.3 Analysis of variance of SN ratio

Source	DF	Seq SS	Adj. SS	Adj. MS	F	P	Percentage Contribution
Alkali concentration	3	2.7238	2.7238	0.90792	19.41	0.018	11.4
Acid concentration	3	1.4815	1.4815	0.49383	10.56	0.042	6.2
L/S ratio	3	1.1344	1.1344	0.37813	8.08	0.060	4.7
Temperature	3	18.5956	18.5956	6.19852	132.50	0.001	77.7
Residual error	3	0.1403	0.1403	0.04678			
Total	15	24.0756					

4.2 Classical approach of optimization for NaOH fallowed by $HClO_4$:

4.2.1 Effect of alkali concentration

In this step we have determined the optimum value of NaOH by taking it in a different concentration of 0.5, 1.5, 2.5, 3.5 mol/L. Water wash SPL was treated with NaOH of concentration at 5 L/S, at a temperature of 50 °C and at 120 rpm for a 4 h. From the figure 8 it was shown that leaching percentage was increased as the alkali concentration from 0.5 - 1.5 mol/L but after 1.5 mol/L the leaching percentage was slightly increases. This was because at 1.5 M NaOH concentration, it provided the required amount of OH^- sites for the dissolving of unleached cryolite (Na_3AlF_6), alumina (Al_2O_3) fractions in the SPL sample.

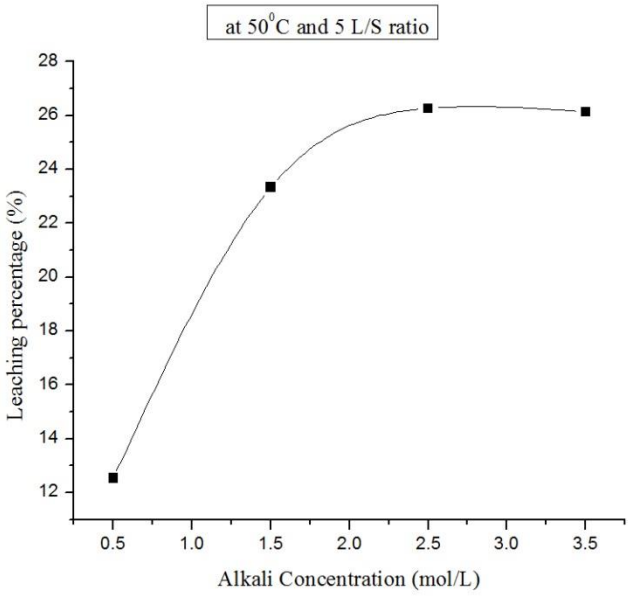


Figure 4.4: Influence of alkali concentration on leaching percentage

4.2.2 Effect of acid concentration:

In this step we have determined the optimum value of $HClO_4$ by taking it in a different concentration of 0.5, 1.5, 2.5, 3.5 mol/L. The optimum value obtained in the alkali leaching was 1.5 M NaOH. The SPL sample obtained from the alkali leaching of 1.5 M NaOH was treated with $HClO_4$ of concentration 2.5, 5.0, 7.5, 10 mol/L with setting parameters of 5 L/S ratio, 50 °C temperature, 120 rpm and 4 h. From the figure 4.5 it is well understood that leaching percentage increases as the acid concentration from 2.5 - 10 mol/L but increment is not that of significant as the maximum 3.87 % increase in the leaching percentage. Finally we have taken 2.5 mol/L taken as the optimized value considering cost as well and output value.

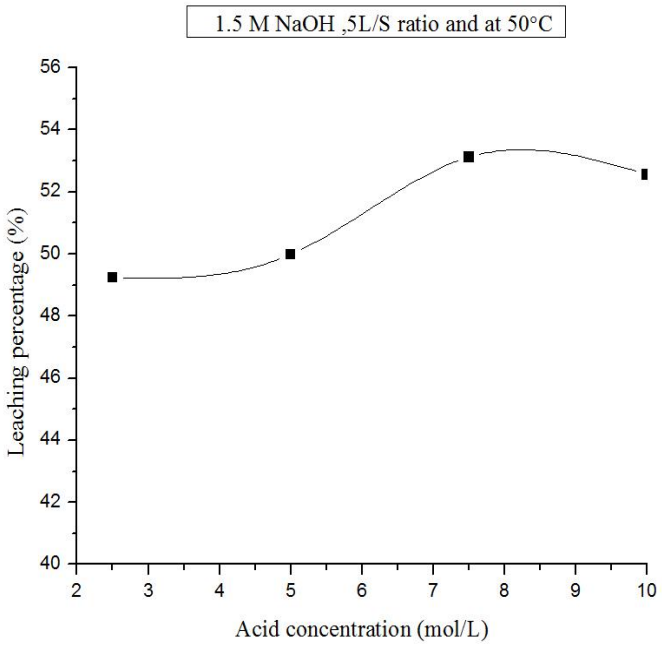


Figure 4.5 Influence of acid concentration on leaching percentage

4.2.3 Effect of L/S ratio:

The water wash SPL sample taken for the alkali leaching. SPL samples were leached in 1.5M NaOH followed by 2.5M $HClO_4$ solution for 4 h at 50 °C, and the L/S ratio varied in the range of 1.5-4.5 cm^3/g. In figure 10 the total leaching percentage obtained after both alkali and acid leaching is shown. It can be seen that the leaching percentage of soluble compounds increases with increasing the L/S ratio in the range of 1.5-4.5. When the L/S goes up to 2.5, the increase of L/S ratio has very less effect on the leaching percentage. This is because increasing L/S ratio provides a mass of OH^- to react with the soluble Na_3AlF_6 and Al_2O_3 in the L/S ratio range of 1.5-2.5. The concentration of soluble Na_3AlF_6 and Al_2O_3 in the leaching solution decreases with the increase of L/S ratio, which makes the leaching percentage gradually constant with further increase in L/S ratio in case of alkali leaching. Similarly in the case of acid leaching the increment in leaching percentage was because of the mass of ClO_4^- to react with the sparingly soluble CaF_2 and $NaAl_{11}O_{17}$ in the range 1.5-2.5.

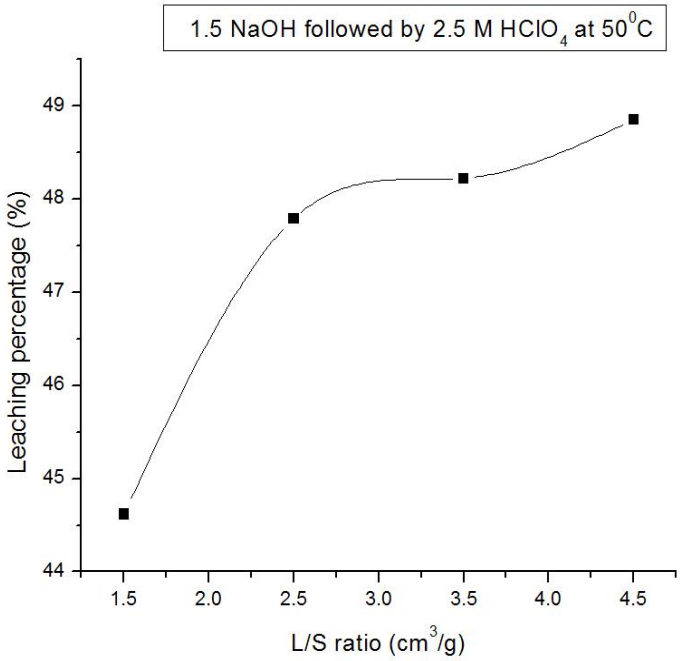


Figure 4.6 Influence of L/S on leaching percentage

4.2.4 Effect of temperature:

SPL samples were leached in 1.5 M NaOH followed by 2.5 M $HClO_4$ solution for 4 h and 2.5 L/S at a different temperature range of 25, 50, 75 and 100 °C. It was observed that the temperature has an appreciable effect on the leaching percentage. The leaching percentage increases from 30.62 % to 54.04 % when the temperature increases from 25 °C to 100 °C.

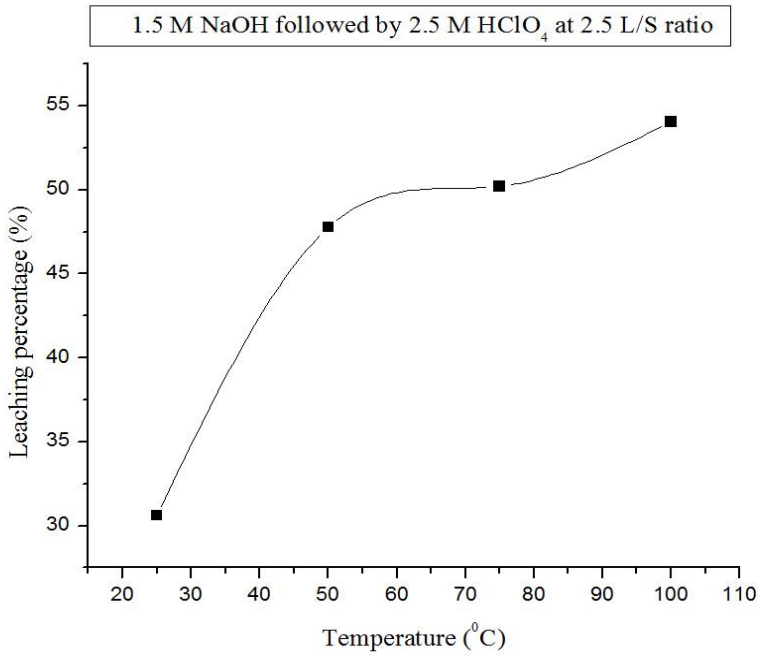


Figure 4.7 Influence of temperature on leaching percentage

4.2.5 Cryolite precipitation:

In order to check the feasibility of the cryolite precipitation the leachates were analyzed at two different pH values. At pH 4.5 the aluminium ions have existed in the form of $Al(OH)_4^-$ or $[Al_8(OH)_{26}]^{2-}$ leading to precipitation of cryolite. While at pH 9.5 Cl^- prevails over the precipitation of cryolite leading to formation of NaCl as confirmed from XRD analysis.

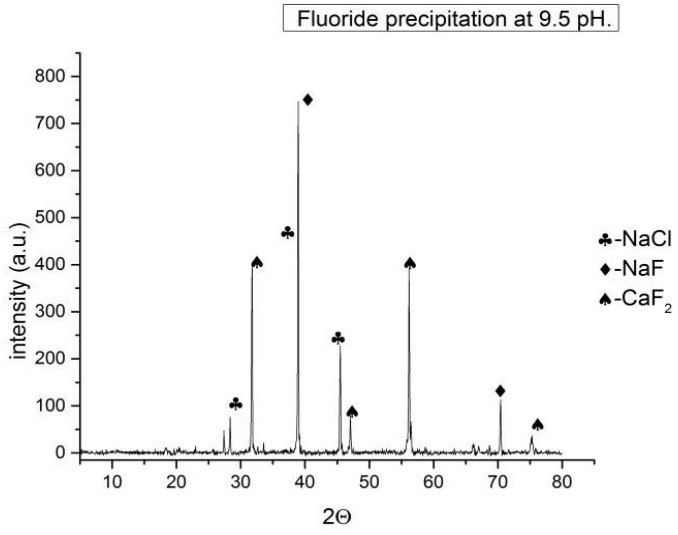


Figure 4.8 XRD analysis of fluoride precipitation at pH value of 9.5

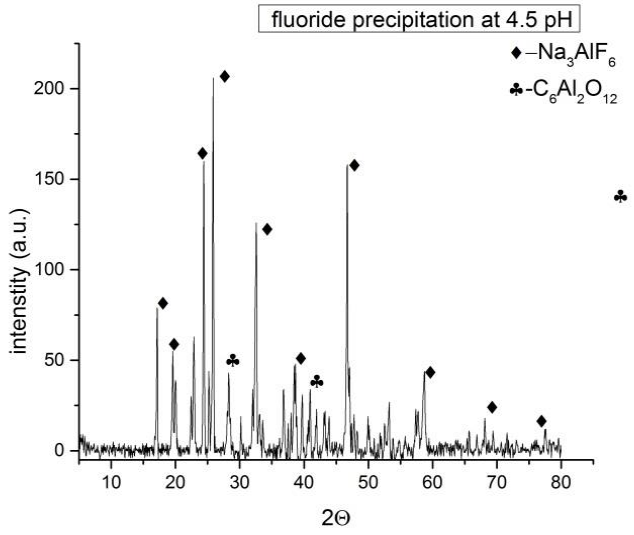


Figure 4.9 XRD analysis of fluoride precipitation at pH value of 4.5

4.3 Characterization of raw and treated sample:

4.3.1 Thermo gravimetric Analysis/DSC:

Thermo gravimetric analysis on SPL samples was performed in a thermo gravimetric analyzer by heating samples up to900 ^{0}C (heating percentage 10 ◦C/min) under N_2 flow (100 ml/min) and O_2 (35 ml/min). Initial sample size was kept constant at 5 mg for N_2 flow and 14.154 mg for O_2flow. The gain in weight in the TGA graph may be due to two reasons i.e.

(i) Chemical reaction (reactions with gaseous substances in the purge gas such as O_2, CO_2 with the formation of non-volatile or hardly volatile compounds).

(ii) Physical transitions (adsorptions of gaseous substances on samples such as active charcoal).

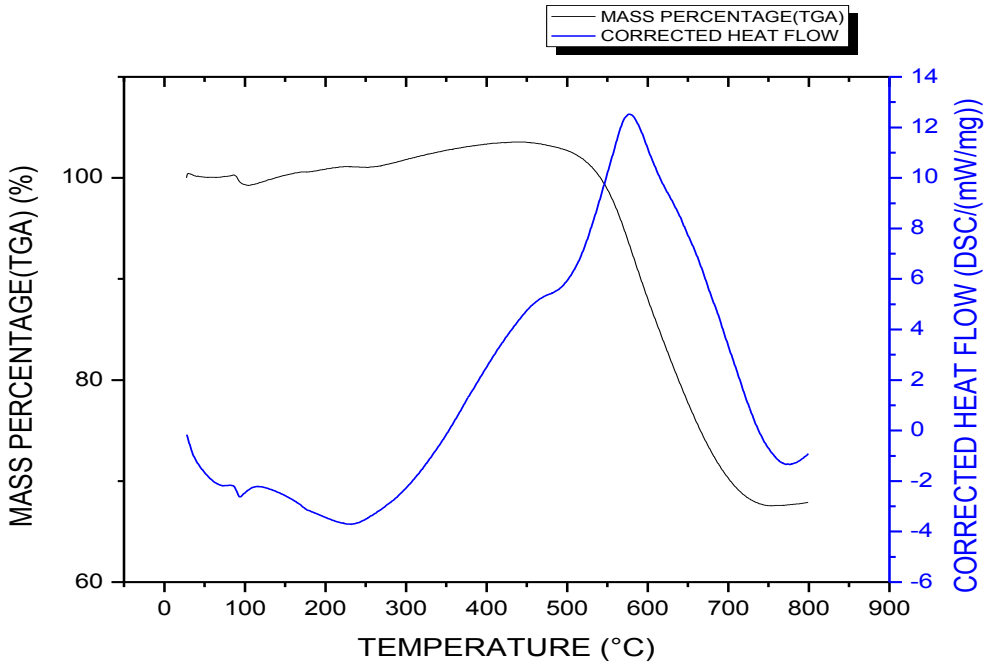


Figure 4.10 TGA under N_2 flow

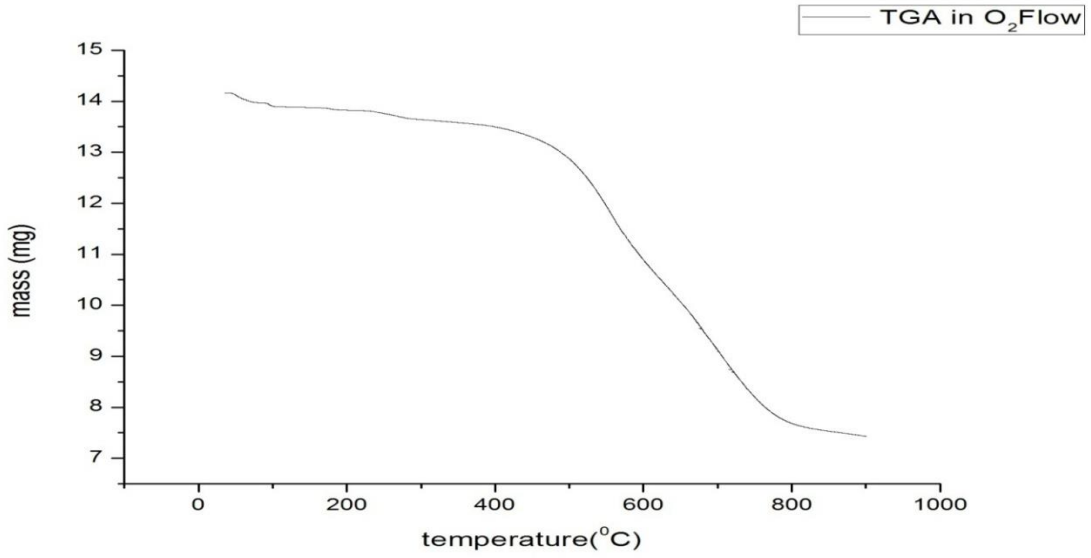


Figure 4.11 TGA under O_2 flow

4.3.2 XRD analysis:

The optimum sample along with that of raw SPL was done and the peaks of graphitic carbon (C), Cryolite (Na_3AlF_6), villaumite (NaF), Fluorite (CaF_2), Sodium Iron Cyanide ($Na_4Fe(CN)_6$), Gibbsite ($Al(OH)_3$) phases were found.

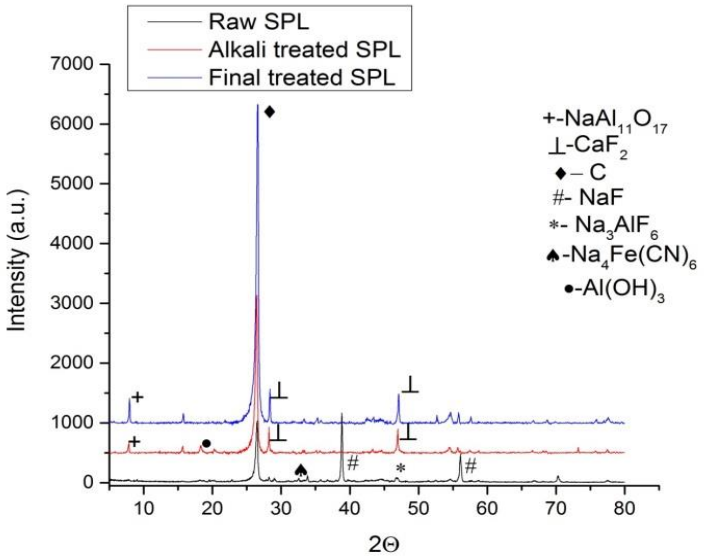


Figure 4.12 XRD analysis of Raw SPL, Treated SPL with NaOH and treated SPL with NaOH fallowed by $HClO_4$

4.3.3 Ultimate and Proximate analysis

The proximate and ultimate analysis were done on the SPL samples as well as on the optimized samples of the samples obtained from the experiments. It was found that the carbon percentage increased upon subsequent treatment.

Table 4.4 Proximate analysis of SPL samples

Sample	Moisture content (%)	Residue content (%)	Volatile matter (%)	Fixed carbon (%)
Raw SPL	3.46	51.89	6.18	38.46
Water Washed SPL	2.40	51.32	5.91	40.37

Alkali treated SPL	2.20	25.25	4.78	67.77
Final treated SPL(NaOH fallowed by $HClO_4$)	2.10	14.84	0.20	82.86

Table 4.5 Ultimate analysis of SPL samples

Component	**Weight percentage (%)**			
	C	**H**	**N**	**S**
Raw SPL	42.19	0.616	0.59	1.24
Water Washed SPL	48.08	0.211	0.40	1.72
Alkali treated SPL (NaOH)	72.01	0.154	0.55	2.46
Final treated SPL (NaOH fallowed by $HClO_4$)	87.03	0.21	0.64	2.67

4.3.4 Particle size analysis by DLS:

The size distribution of raw SPL is done in water and the profile is shown below.

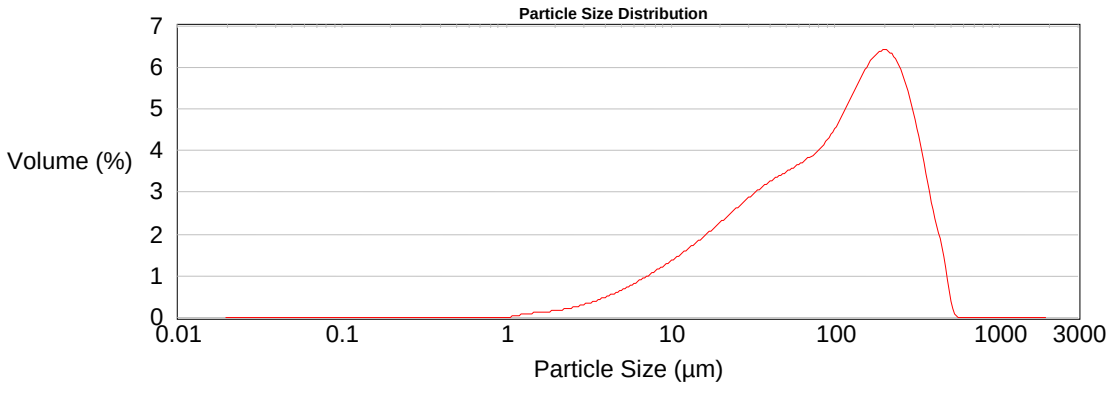
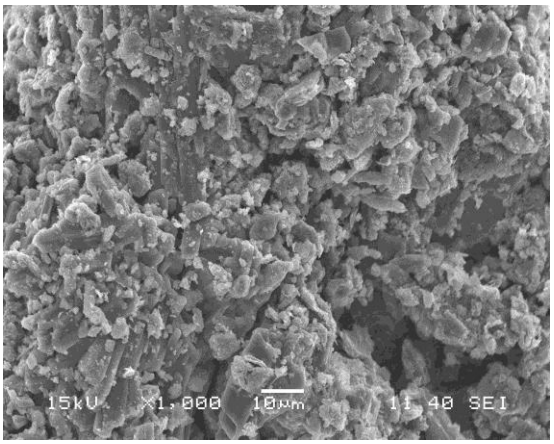


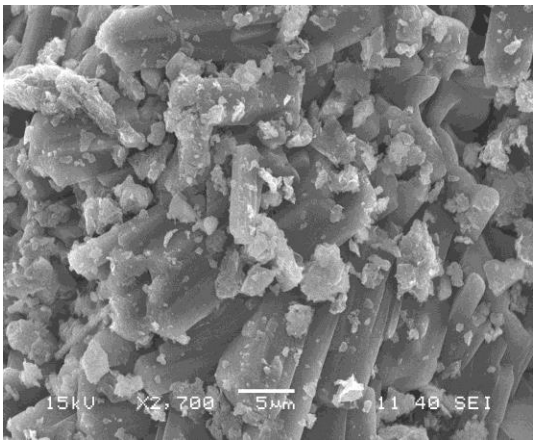
Figure 4.13 Particle size analysis of raw SPL

D minimum = 13.964 μm
D mean = 102.136 μm
D Max = 296.079 μm

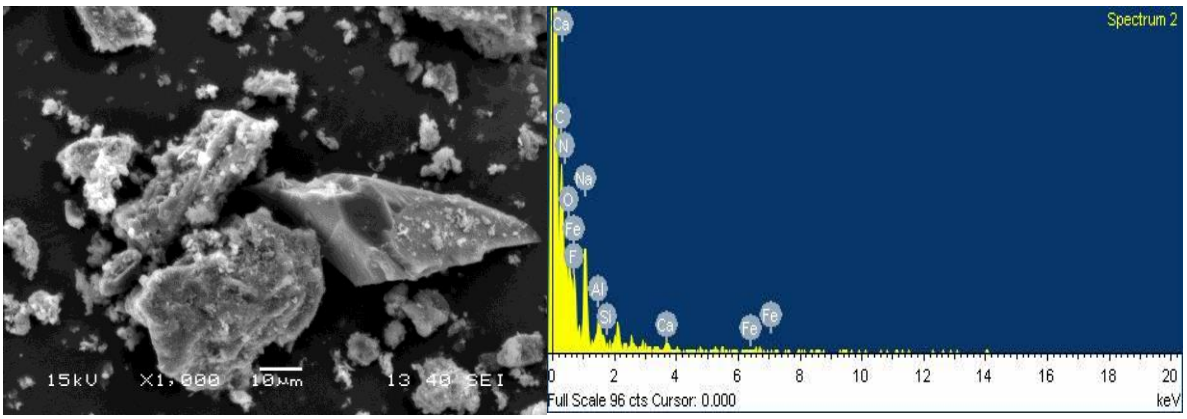
4.3.5 SEM- EDX analysis:



(i)

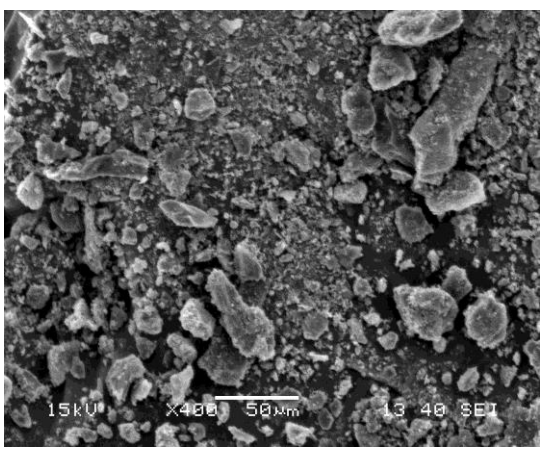


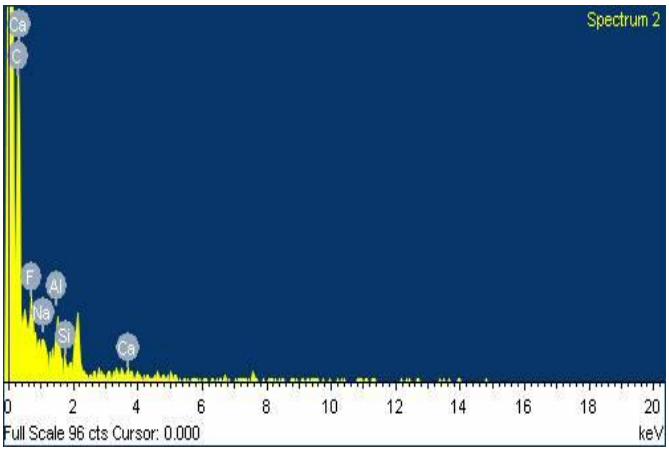
(ii)



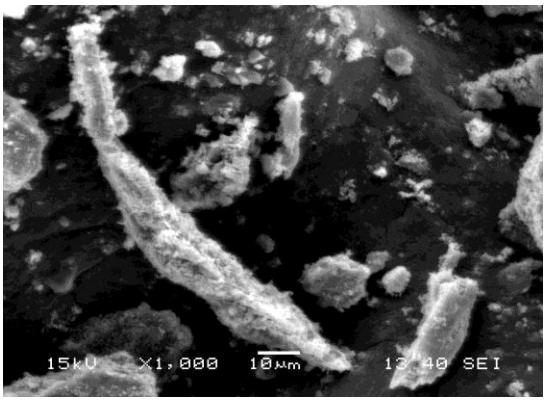
(iii) (iv)

Figure 4.14 SEM-EDX images of raw SPL (i, ii, iii, iv)



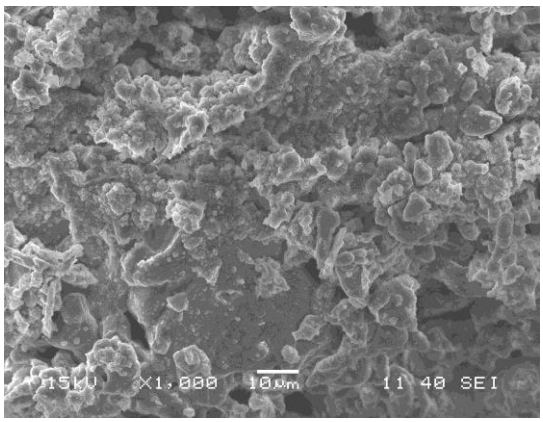


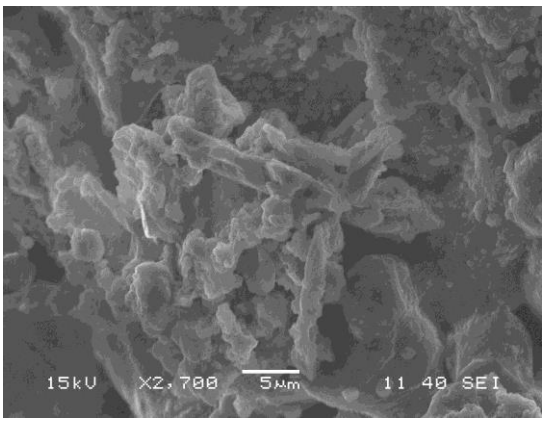
(i) (ii)



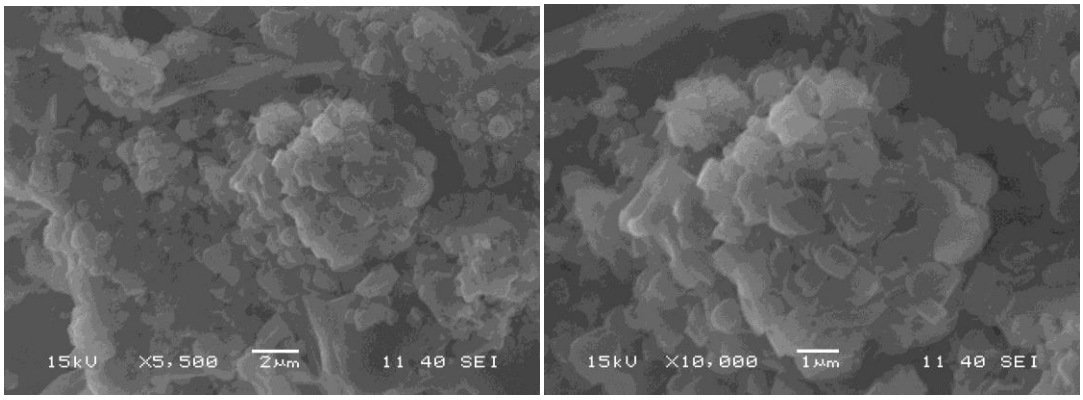
(iii)

Figure 4.15 SEM-EDX images of water wash SPL (i, ii, iii)

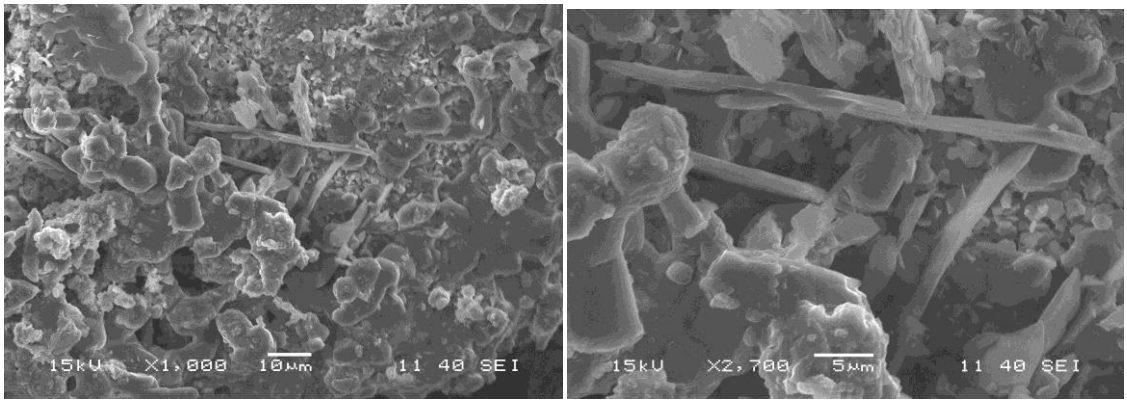




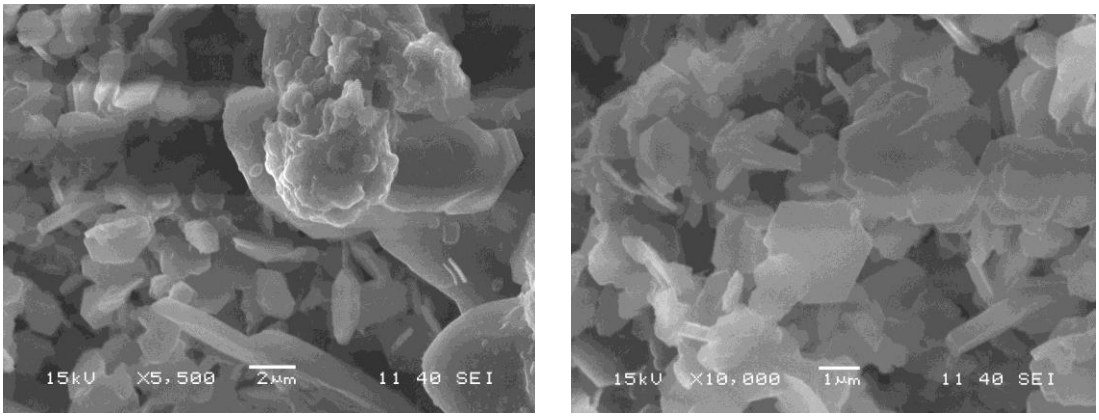
(i) (ii)



(iii) (iv)

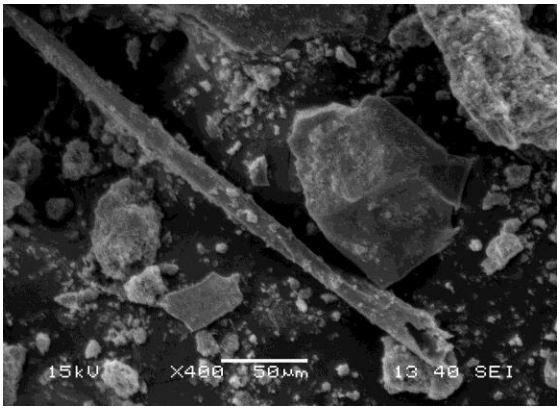


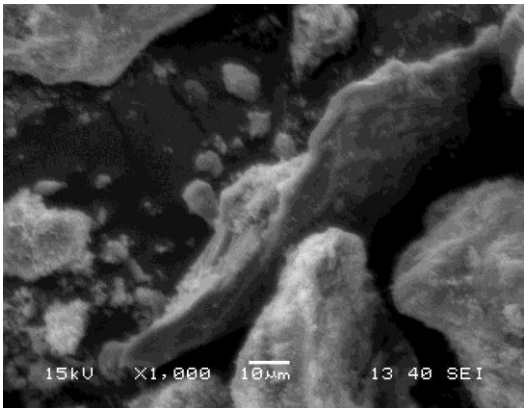
(v) (vi)



(vii) (viii)

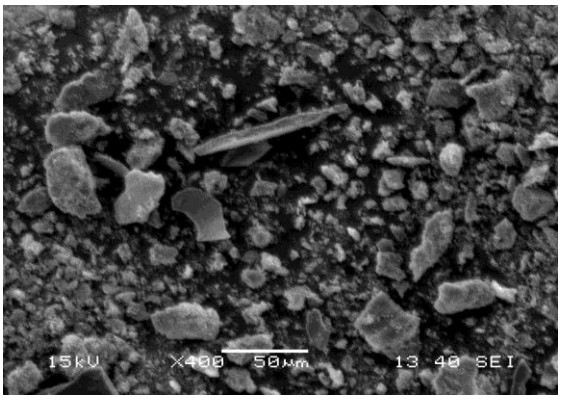
Figure 4.16 SEM images Raw SPL sample burned at 750^{0}C for 1.5h (i, ii, iii, iv) and at 800 ^{0}C(v, vi,vii, viii) for 5h.

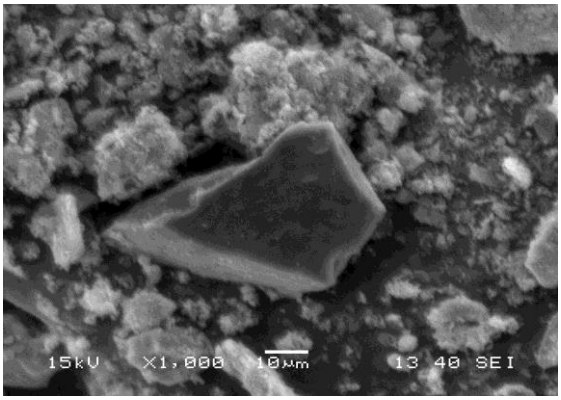




(i) (ii)

Figure 4.17 SEM images of alkali treatment SPL at 1.5 M NaOH (i, ii)





(i) (ii)

Figure 4.18 SEM images of alkali followed by acid treatment SPL1.5 MNaOH+2.5M $HCLO_4$ (i, ii)

The 300µm size fraction shows SPL particles mainly comprising carbonaceous material with finely divided inorganics attached to the exposed surfaces; this agrees with the hypothesis that breakage occurs along the inside layers of bath material between the layers of graphene**.**An illustrative particle can be seen in the top left-hand side corner of Figure 4.16 ii, v, vi, vii with thin needle-like inorganic compounds intercalated by exfoliation of the graphene layer together with inorganic coating on the outer perimeter.

Figure 4.15 i, ii, iii shows partial mineral liberation of the inorganic materials from the carbon fraction. Some elongated graphite particles (dark color) appeared completely liberated at this size fraction, thus contrasting with finely divided inorganics (brighter colored particles) attached to graphite particles or as independent units. The observed partial liberation of graphite

and inorganics below 300 μm agreed well with observations on mineral liberation from SPL samples. Figure 19 i, ii offers a closer look to partially liberated graphite particles reflecting the fact that most of the inorganics that remained attached to graphite were in the form of a relatively thin layer (~1 μm) that was fully accessible to any leaching solution.

4.3.6 Calorific value analysis:

The heat of combustion (calorific value) of raw SPL, water wash SPL, treated water wash SPL with 1.5 M NaOH, treated sample with 1.5 M NaOH followed by 2.5 M $HClO_4$ and treated sample with 1.5 M NaOH followed 2.5 M $HClO_4$ were done with Parr 6100 calorimeter. The results are tabulated in the table 4.6.

Table 4.6 Calorific values of Samples

Compounds	**Calorific value (cal/g)**
Raw SPL	2865.0418
Water wash SPL	3924.8990
Alkali treated SPL	5057.5625
Final treated SPL (NaOH fallowed by $HClO_4$)	6533.6473

4.4 Response Surface Methodology of NaOH fallowed by $HClO_4$:

A four factor and two level full factorial central composite design having alpha value 1 was used to determine the optimal factors of leaching percentage for the chemical treatment of Spent Pot Lining.

The study was carried according to the central composite design and the experimental points used according to the design are shown in Table 4.7.

A second-order polynomial equation was used to express the leaching percentage as a function of independent variables.

$$y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 + b_{11}x_1^{\,2} + b_{22}x_2^{\,2} + b_{33}x_3^{\,2} + b_{44}x_4^{\,2} + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{14}x_1x_4 + b_{23}x_2x_3 + b_{24}x_2x_4 + b_{34}x_3x_4$$

Table 4.7 The central composite design with four independent variables and experimental leaching percentage

Sl.no.	Alkali concentration (mol/L)	Acid concentration (mol/L)	L/S ratio (cm^3/g)	Temperature (^0C)	Leaching percentage	Fitted
1.	2.0	6.25	3.0	25.0	37.41	37.424
2.	3.5	10.00	4.5	25.0	40.57	41.230
3.	3.5	10.00	1.5	25.0	35.40	35.579
4.	2.0	6.25	3.0	25.0	37.41	37.424
5.	2.0	10.00	3.0	25.0	38.75	38.332
6.	0.5	10.00	1.5	25.0	32.14	31.865
7.	2.0	6.25	3.0	25.0	37.64	37.424
8.	3.5	6.25	3.0	25.0	36.88	36.549
9.	2.0	6.25	3.0	25.0	37.05	37.424
10.	0.5	2.50	1.5	62.5	35.70	34.992
11.	2.0	6.25	1.5	62.5	41.55	42.111
12.	0.5	2.50	1.5	62.5	34.11	34.992
13.	2.0	6.25	4.5	62.5	48.53	48.865
14.	2.0	6.25	3.0	62.5	45.55	46.488
15.	2.0	2.50	3.0	62.5	40.22	41.534
16.	3.5	2.50	1.5	62.5	36.74	35.639
17.	3.5	10.00	1.5	62.5	43.92	44.738
18.	3.5	10.00	4.5	62.5	54.17	53.112
19.	2.0	6.25	3.0	62.5	47.60	46.488
20.	0.5	2.50	4.5	62.5	40.27	40.127
21.	2.0	6.25	3.0	62.5	47.02	46.488
22.	3.5	2.50	4.5	62.5	44.70	40.127
23.	3.5	2.50	4.5	100.0	49.11	49.924
24.	2.0	6.25	3.0	100.0	47.50	47.279
25.	0.5	2.50	4.5	100.0	41.90	40.822
26.	0.5	10.00	4.5	100.0	39.88	39.832
27.	0.5	6.25	3.0	100.0	38.77	39.997
28.	3.5	2.50	1.5	100.0	38.12	38.333
29.	0.5	10.00	1.5	100.0	33.04	32.471

30.	0.5	10.00	4.5	100.0	39.12	39.832
31.	2.0	6.25	3.0	100.0	48.33	47.279

The experimental values for leaching percentage under different conditions are presented in Table 4.7. The regression coefficients for the second order polynomial equation and results for the linear, quadratic and interaction term are presented in table 4.8. The statistical analysis indicates that the model was adequate, processing no significant lack of fit and with very satisfactory of the actual R^2 (.9826) to that of predicted value of .9006 and adjusted R^2 value of (.9673). The closer the value of R^2 to unity the better the empirical model fits the actual data.

Table 4.8 Regression coefficient, p or probability for leaching percentage

Variables	Reg. coefficient	Standard Deviation	t- value	P
Constant	46.4878	0.4440	104.709	0.000
Acid concentration	3.2037	0.2998	10.686	0.000
Alkali concentration	2.4791	0.2997	8.271	0.000
L/S ratio	3.3769	0.2618	12.899	0.000
Temperature	4.9278	0.2962	16.638	0.000
Acid concentration* Acid concentration	-1.7183	0.6979	-2.462	0.026
Alkali concentration* Alkali concentration	-2.4746	0.6115	-4.046	0.001
L/S ratio* L/S ratio	-0.9997	0.6444	-1.551	0.140
Temperature* Temperature	-0.1360	0.5568	-7.428	0.000
Acid concentration *	1.9476	0.3468	5.614	0.000

Alkali concentration				
Acid concentration * L/S ratio	0.9335	0.2816	3.315	0.004
Acid concentration* Temperature	2..3604	0.4854	4.862	0.000
Alkali concentration* L/S ratio	-0.1237	0.2623	-0.472	0.644
Alkali concentration* temperature	-0.9035	0.5445	-1.659	0.116
L/S ratio* temperature	1.3611	0.4083	3.334	0.006

S = 0.976852 PRESS = 87.1611

R^2 = 98.26% R^2(pred) = 90.06% R^2(adj) = 96.73%

4.4.1 Analysis of variance:

The reason of performing the analysis of variance (ANOVA) is to investigate which design parameters significantly affect the quality characteristics. From the data, there is a tool called an "F test" termed after Fisher to see which design parameters have a significant effect on the quality characteristic. The F value for each design parameter is simply the ratio of mean of squared deviations to the mean of squared error. Generally when F>4 indicates that the design parameter has a significant effect on the quality characteristics. Table 4.9 shows the results of ANOVA for leaching percentage at various process and reaction conditions. From the table 4.9 it pretty well understood that alkali concentration is having least significance on leaching percentage whereas acid concentration is having most effect on the leaching percentage.

Table 4.9 ANOVA for leaching percentage using Adjusted Sum of Squares (SS) for tests

Source	DF	Seq. SS	Adj. SS	Adj.MS	F	P
Regression	14	861.367	861.367	61.526	64.48	0.000
Linear	4	485.510	657.369	164.342	172.22	0.000
Acid Concentration	1	110.906	108.963	108.963	114.19	0.000
Alkali Concentration	1	0.836	65.280	65.280	68.41	0.000
L/S ratio	1	253.350	158.763	158.763	166.38	0.000
Temperature	1	120.418	264.163	264.163	276.83	0.000
Square	4	261.396	163.765	38.441	40.28	0.000
Acid concentration* Acid concentration	1	136.306	5.784	5.764	6.06	0.026
Alkali concentration* Alkali concentration	1	0.985	15.625	15.625	16.37	0.001
L/S ratio* L/S ratio	1	14.521	2.297	2.297	2.41	0.140
Temperature* Temperature	1	109.585	52.648	52.648	55.17	0.000
Interaction	6	114.460	114.460	19.077	19.99	0.000
Acid concentration * Alkali concentration	1	26.735	30.076	30.076	31.52	0.000
Acid concentration * L/S ratio	1	19.572	10.487	10.487	10.99	0.004
Acid concentration* Temperature	1	49.998	22.562	22.562	23.64	0.000
Alkali concentration* L/S ratio	1	3.206	0.212	0.212	0.22	0.644
Alkali concentration* temperature	1	4.345	2.628	2.628	2.75	0.116
L/S ratio* temperature	1	10.604	10.604	10.604	11.11	0.004
Residual error	16	15.268	15.268	0.954	2.54	0.104
Lack of fit	10	10.959	10.959	1.370		
Pure error	6	4.390	4.309	0.539		

Total	30	876.635				

Effect of acid and alkali concentration, L/S ratio and temperature has been investigated by Response Surface Methodology. The levels of independent parameters were based on preliminary experiments.

$$y = 46.4878 + 3.2037x_1 + 2.4791x_2 + 3.3769x_3 + 4.9278x_4 - 1.7183x_1^{\,2} - 2.4746x_2^{\,2} - 0.9997x_3^{\,2} - 0.1360x_4^{\,2} + 1.9476x_1x_2 + 0.9335x_1x_3 + 2.3604x_1x_4 - 0.1237x_2x_3 - 0.9035x_2x_4 + 1.3611x_3x_4$$

4.4.2 Contour Plot and Surface plot:

These plots is done for finding the response in both the two-dimensional as well as three-dimensional in which the setting that produce the same response are shown as contour lines of constant responses. From the figure it is well understood that the leaching percentage increases with increase in acid concentration and L/S ratio.

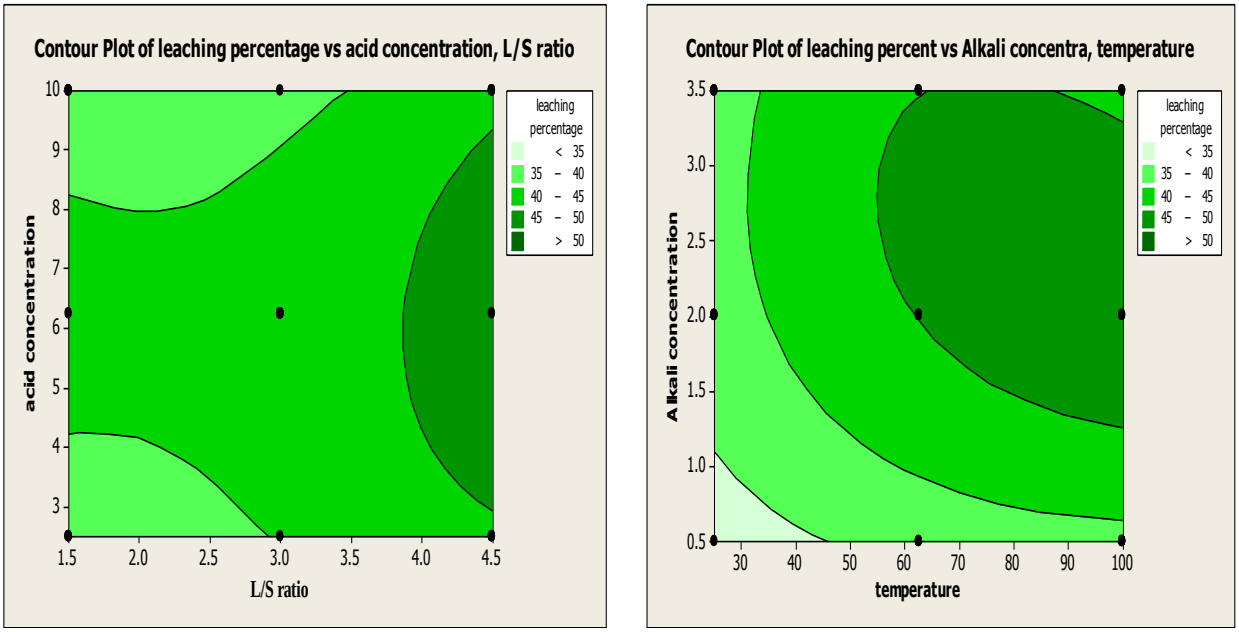


Figure 4.19 Contour plot of leaching percentage vs acid concentration L/S ratio & Contour plot of leaching percentage vs alkali concentration, temperature

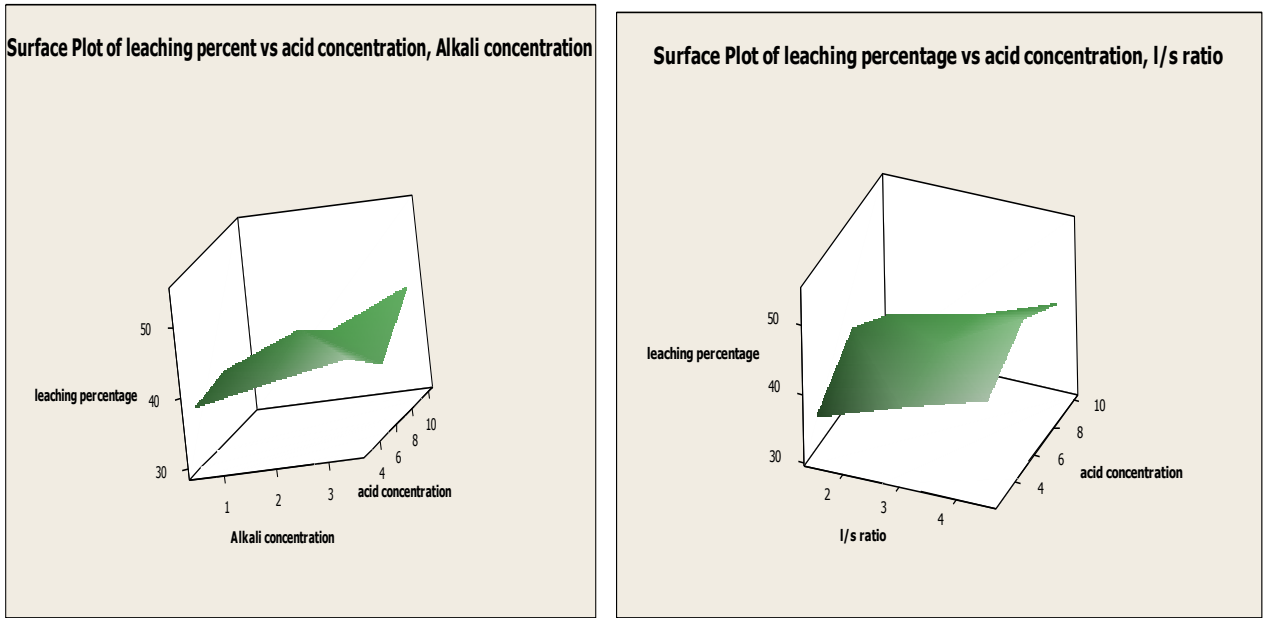
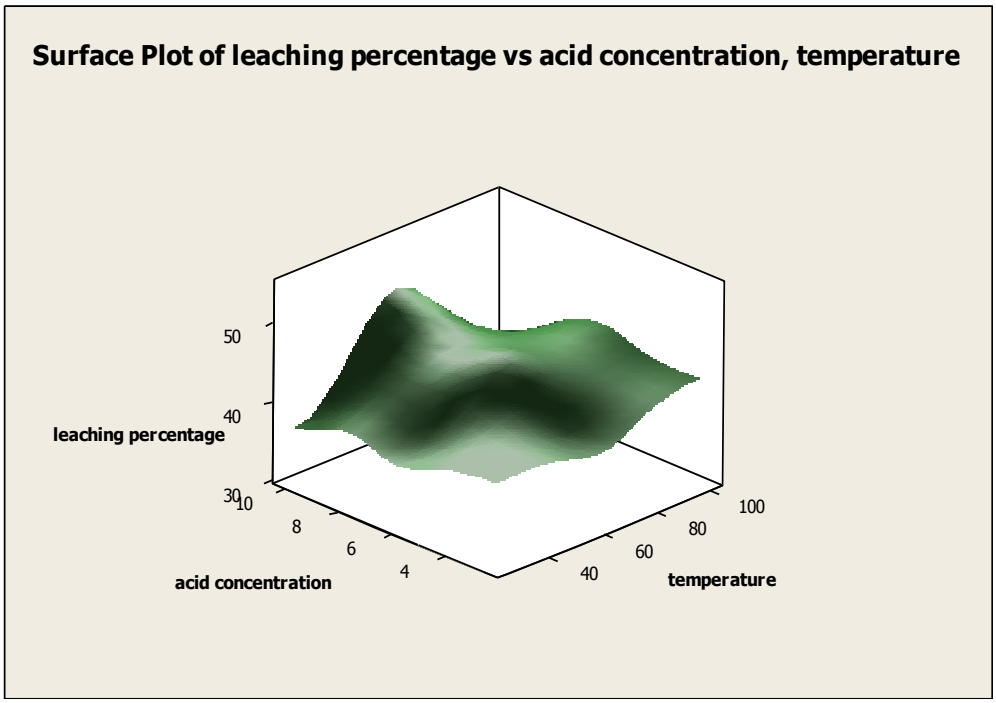


Figure 4.20 Surface plot for leaching percentage vs acid concentration, alkali concentration & Surface plot for leaching percentage vs acid concentration, L/S ratio



Fgure 4.21 Surface plot for leaching percentage vs acid concentration, temperature

4.4.3 Residual plot:

The four-in-one residual plot displays four different residual plots together in one graph window. This layout can be useful for comparing the plots to determine whether your model meets the assumptions of the analysis. The residual plots in the graph include:

- Histogram – indicates whether the data are skewed or outliers exist in the data

- Normal probability plot – indicates whether the data are normally distributed, other variables are influencing the response, or outliers exist in the data

- Residuals versus fitted values – indicates whether the variance is constant, a nonlinear relationship exists, or outliers exist in the data

- Residuals versus order of the data – indicates whether there are systematic effects in the data due to time or data collection order

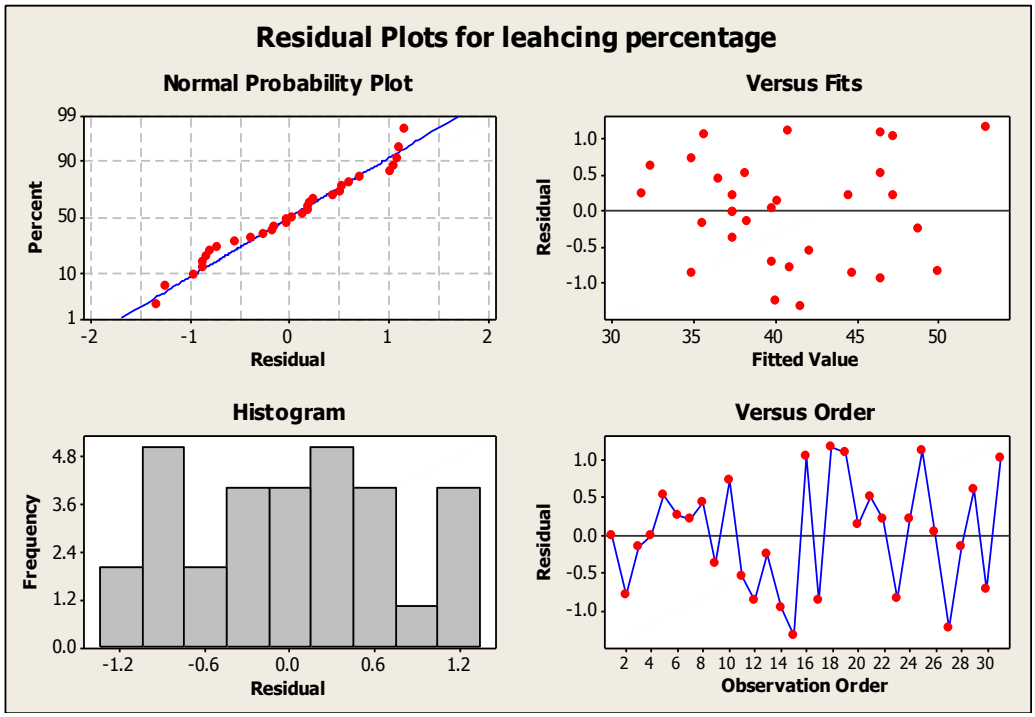


Figure 4.22 Residual plot for leaching percentage

PART 2:

4.5 Taguchi optimization of NaOH fallowed by H_2SO_4:

The main objective for the optimization was to know the effect of acid concentration, alkali concentration, temperature, L/S on the leaching percentage in terms of percentage contribution. Table 14 shows the experimental results for leaching percentage of water washed SPL with that of H_2SO_4 at different setting parameters with corresponding to S/N ratio.

Table 4.10 Taguchi design of NaOH fallowed by H_2SO_4

Sl. no.-	Alkali concentration (M)	Acid concentration (M)	L/S ratio (cm^3/g)	Temperature (°C)	Actual Leaching percentage (%)	Actual SN ratio	Predicted leaching percentage (%)	Predicted SN ratio
1	0.5	2.5	1.5	25	29.50	29.3964	32.6594	30.1241
2	1.5	7.5	4.5	25	51.37	34.2142	51.2044	34.1447
3	2.5	10.0	2.5	25	48.27	33.6735	48.2219	33.6009
4	3.5	5.0	3.5	25	52.39	34.3850	49.4444	33.7994
5	0.5	5.0	2.5	50	41.77	32.4173	41.6044	32.3478
6	1.5	10.0	3.5	50	49.52	33.8956	52.6794	34.6233
7	2.5	7.5	1.5	50	50.70	34.1002	47.7544	33.5146
8	3.5	2.5	4.5	50	48.49	33.7130	48.4419	33.6404
9	0.5	7.5	3.5	75	45.50	33.1602	45.4519	33.0876
10	1.5	2.5	2.5	75	48.93	33.7915	45.9844	33.2059
11	2.5	5.0	4.5	75	49.34	33.8640	52.4994	34.5916
12	3.5	10.0	1.5	75	47.72	33.5740	47.5544	33.5045
13	0.5	10.0	4.5	100	50.28	34.0279	47.3344	33.4423
14	1.5	5.0	1.5	100	48.45	33.7059	48.4019	33.6333
15	2.5	2.5	3.5	100	50.32	34.0348	50.1544	33.9653
16	3.5	7.5	2.5	100	49.52	33.8956	52.6794	34.6233

4.5.1 Analysis of the S/N ratio:

The word “signal” represents the desirable value (mean) for the output characteristics, and the word “noise” signifies the undesirable value[standard deviation(SD)] for the output characteristics in Taguchi method. Thus the S/N ratio is the ratio of the mean to the SD. Taguchi method uses the S/N ratio to measure the quality characteristic deviating from the desired value. The “nominal is best”, “larger is better” and “smaller is better” are there categories of quality characteristics in Taguchi method. Here “larger is better” is selected for the optimum leaching percentage calculation. The S/N ratio Y is determined by means of following equation,

$$Y = -10log\sum_{k=1}^{n}\binom{n}{k}x\mathrm{k}^{-2} \qquad \text{(a)}$$

Where n is the number of test and x_k are the comparison variables in the kth experiment.

Table 4.11 Response Table for Signal to Noise Ratios

Level	Alkali concentration	Acid concentration	L/S	Temperature
1	41.76	44.31	44.09	45.38
2	49.57	47.99	47.12	47.62
3	49.66	49.27	49.43	47.87
4	49.53	48.95	49.87	49.67
Delta	7.89	4.96	5.78	4.26
Rank	1	3	2	4

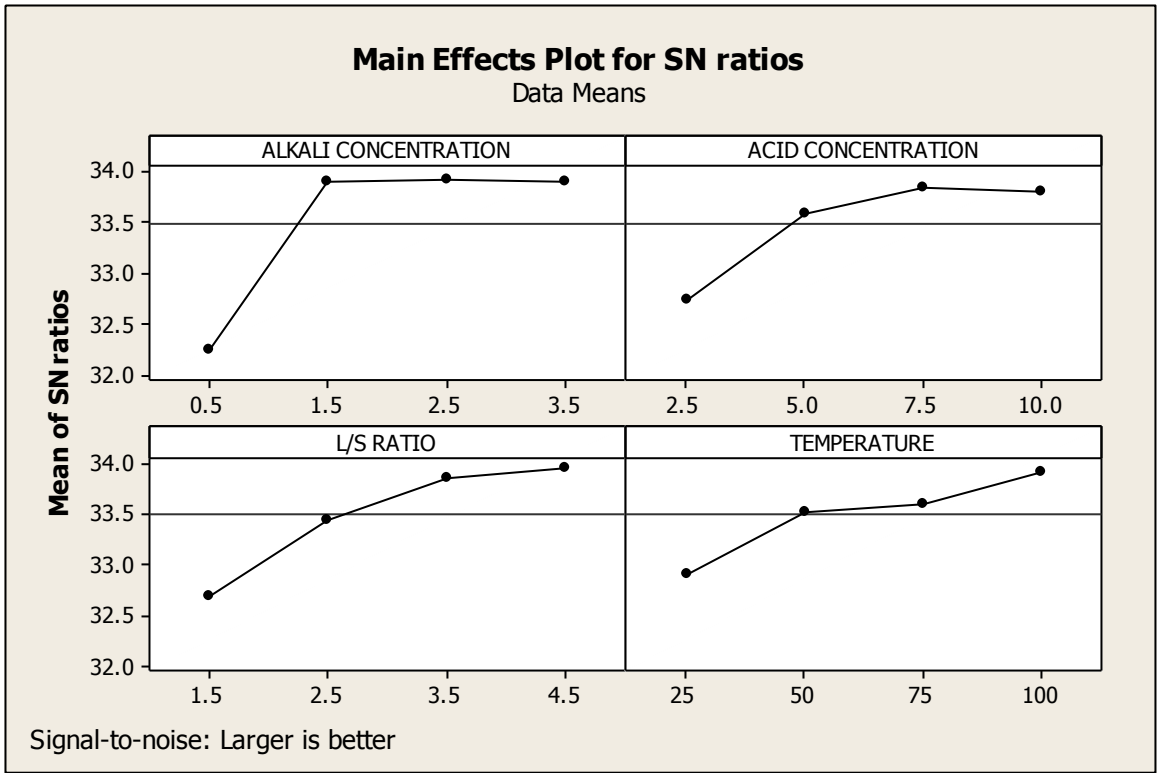


Figure 4.23 Main effect plot for SN ratio

4.5.2 Analysis of variance:

The reason of performing the analysis of variance (ANOVA) is to investigate which design parameters significantly affect the quality characteristics. F test has been conducted to know the significant effect on the quality characteristic. The F value is the ratio of the mean of the squared deviations of the mean of squared errors. Table 4.12 shows the results of ANOVA for leaching percentage at various process and reaction conditions. Once the optimal level of the design parameters has been selected, the final step is to predict and verify the improvement of the quality characteristics using the optimal level of the design parameters.

The estimated S/N ratio using the optimal parameters for leaching percentage can be obtained, and the corresponding other parameters can be calculated by the equation (a). Table 4.10 shows the comparison of the predicted leaching percentage and the actual leaching percentage and the actual S/N ratio with that of Taguchi predicted S/N ratio. Results indicated that there is good agreement between the predicted and actual leaching percentage.

Table 4.12 Analysis of variance for SN ratio

Source	DF	Seq SS	Adj. SS	Adj. MS	F	P	Percentage Contribution
Alkali concentration	3	8.203	8.203	2.7345	2.32	0.253	44.96
Acid concentration	3	3.193	3.193	1.0642	0.90	0.532	18.22
L/S ratio	3	3.980	3.980	1.3268	1.13	0.462	26.31
Temperature	3	2.091	2.091	0.6970	0.59	0.661	11.94
Residual error	3	3.530	3.530	1.1766			

4.6 Classical approach of optimization of NaOH fallowed by H_2SO_4:

4.6.1 Effect of alkali concentration:

In this step we have determined the optimum value of NaOH by taking it in a different concentration of 0.5, 1.5, 2.5, 3.5 mol/L. Water wash SPL is treated with NaOH of concentration at 5 L/S, at a temperature of 50 ^{0}C and at 120 rpm for a 4 hr. the results were plotted in a graph 4.22.

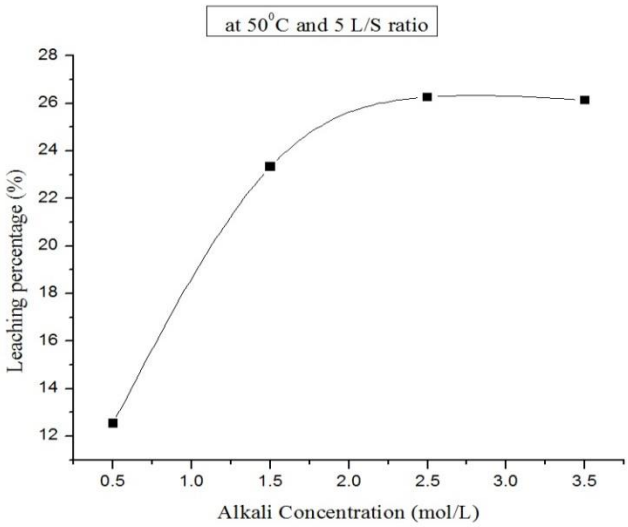


Figure 4.24 Effect of alkali concentration on leaching percentage

From the figure 28 it is seen that leaching percentage is increases as the alkali concentration from 0.5 - 1.5 mol/L but after 1.5 mol/L the leaching percentage is slightly increases. This was because at 1.5 M NaOH concentration leaching it provided the required amount of OH- sites for the dissolving of unleached cryolite (Na_3AlF_6), alumina (Al_2O_3) fractions in the SPL sample.

4.6.2 Effect of acid concentration:

In this step we were determine the optimum value of H_2SO_4 by taking it in a different concentration of 0.5,1, 1.5, 2, 2.5, 5, 7.5 and 10 mol/L. The optimum value obtained in the alkali leaching is 1.5 M NaOH. The SPL sample obtained from the alkali leaching of 1.5 M NaOH was treated with H_2SO_4 of concentration 2.5, 5.0, 7.5, 10 mol/L with setting parameters of 5 L/S ratio, 50 ^{0}C temperature, 120 rpm and 4 hr time .The results are plotted in a table.

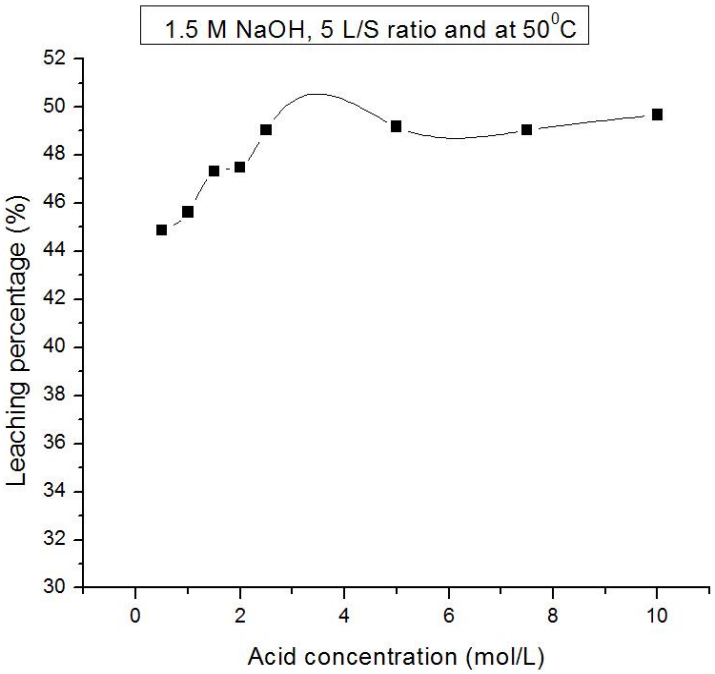


Figure 4.25 Influence of acid concentration on leaching percentage

4.6.3 Optimization of L/S:

The water wash SPL sample taken for the alkali leaching. SPL samples were leached in 1.5 M NaOH followed by 2.5 M H_2SO_4 solution for 4 h at 50 °C, and the L/S ratio varied in the range of 1.5-4.5 cm^3/g. It can be seen that the leaching percentage of soluble compounds increases with increasing the L/S ratio in the range of 1.5-4.5.the result were plotted in fig4.26..

When the L/S goes up to 2.5, the increase of L/S ratio has no more effect on the leaching percentage. This is because increasing L/S ratio provides a mass of OH^- to react with the soluble Na_3AlF_6 and Al_2O_3 in the L/S ratio range of 1.5-2.5 cm^3/g. The concentration of soluble Na_3AlF_6 and Al_2O_3 in the leaching solution decreases with the increase of L/S ratio, which makes the leaching percentage gradually constant with further increase in L/S ratio.

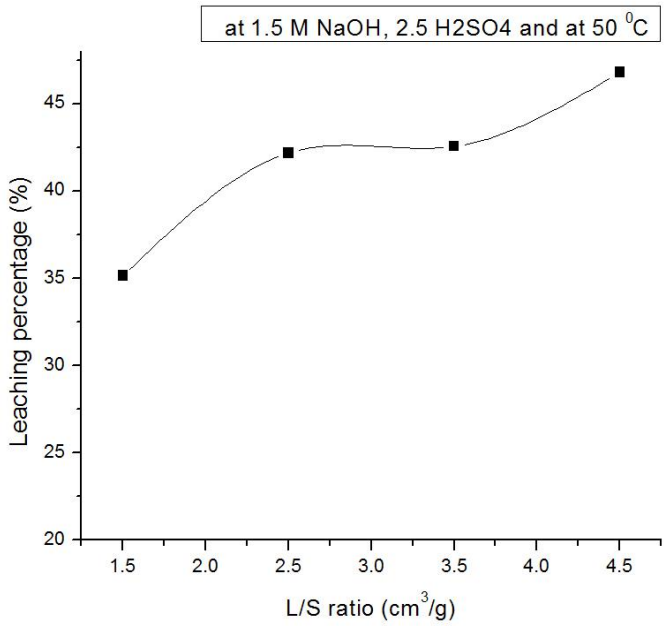


Figure 4.26 Influence of L/S on leaching percentage

The effect of L/S ratio is studied from 1.5-4.5 cm^3/g and from the figure 6 it is observed that there is slight increase in leaching percentage from 1.5-2.5. But after that the leaching percentage shows gradual and steady increment. This increase in leaching percentage is because of the mass of ClO_4^- to react with the sparingly soluble CaF_2 and $NaAl_{11}O_{17}$ in the range 1.5-2.5.

4.6.4 Optimization of temperature:

SPL samples were leached in 1.5 M NaOH followed by 2.5 M H_2SO_4 solution for 4 h and 5 L/S at a different temperature range of 25, 50, 75 and 100 ^0C. It is observed that the temperature has an appreciable effect on the leaching percentage from temperature 25 to 50 ^0C. After that temperature does not affect on leaching percentage because of decreasing the leaching percentage from temperature 50 to 100 ^0C.

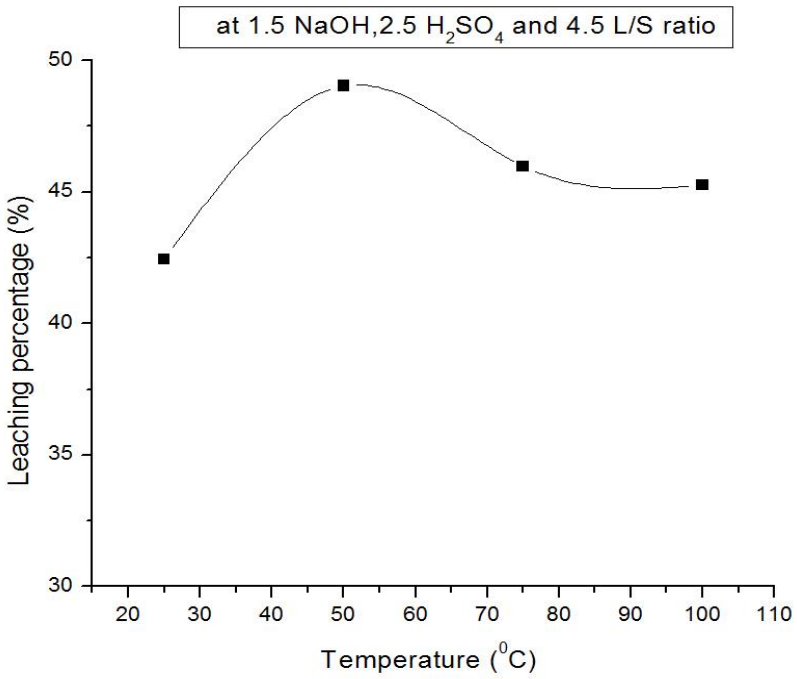


Figure 4.27 Influence of temperature on leaching percentage

4.6.5 XRD analysis:

The optimum sample along with that of raw SPL was done and the peaks of graphitic carbon (C), Cryolite (Na_3AlF_6), villaumite (NaF), Fluorite (CaF_2), Sodium Iron Cyanide ($Na_4Fe(CN)_6$), Gibbsite ($Al(OH)_3$) phases were found.

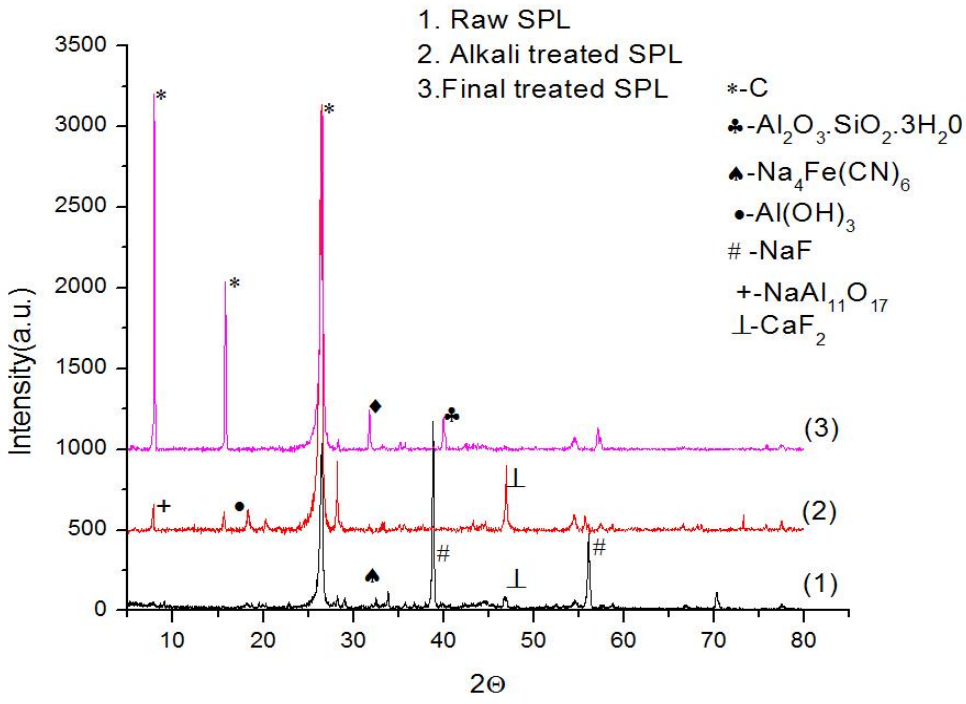


Figure 4.28 XRD analysis of raw SPL, Alkali treated SPL, and treated SPL with NaOH Fallowed by H_2SO_4 samples.

4.6.6 Cryolite precipitation:

In order to check the feasibility of the cryolite precipitation the leachates were analyzed at two different pH values. At pH 4.5 and 9.5 the aluminium ions have existed in the form of $Al(OH)_4^-$ or $[Al_8(OH)_{26}]^{2-}$ leading to precipitation of cryolite. It means both the condition of pH was satisfied for the precipitation of cryolite.

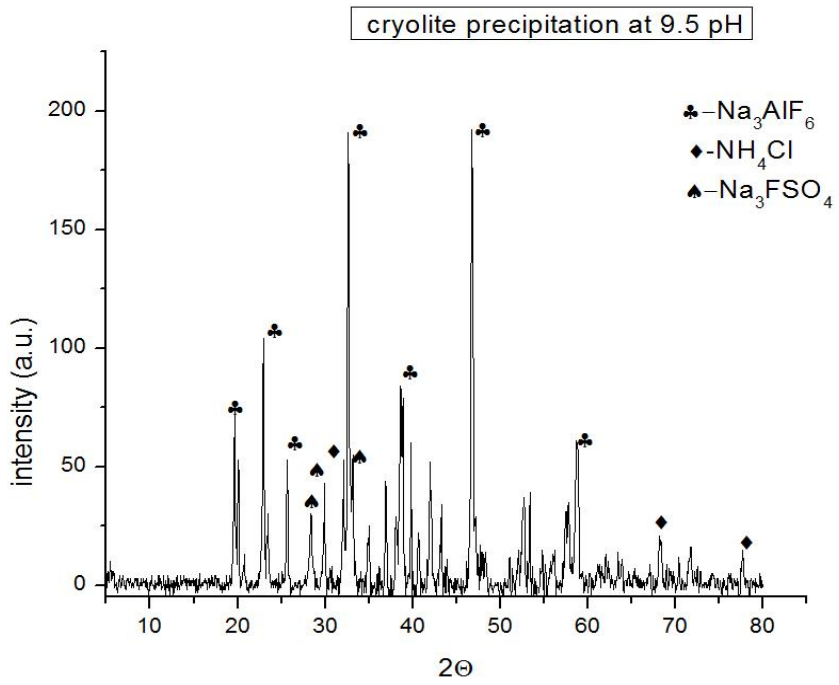


Figure 4.29 XRD analysis of fluoride precipitation at pH value of 9.5

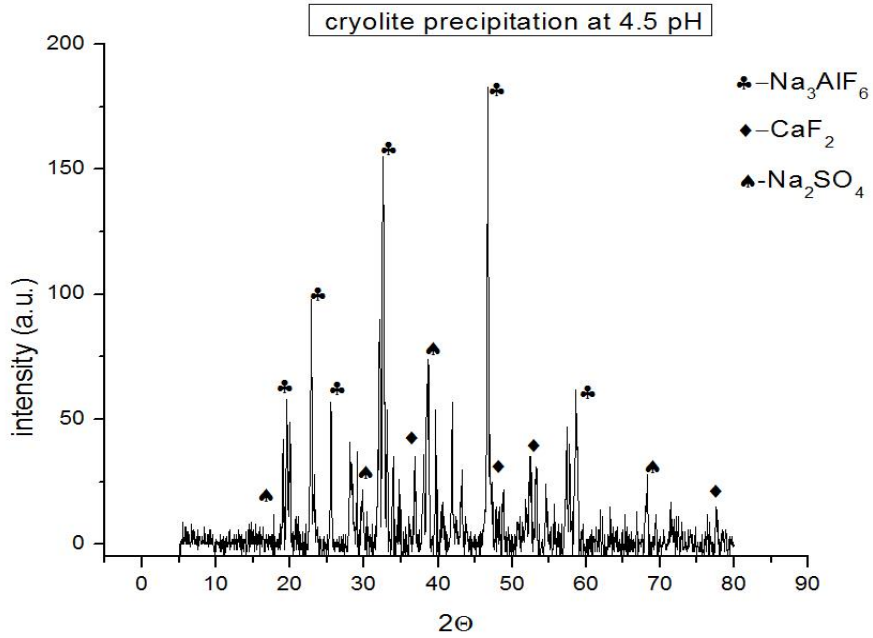


Figure 4.30 XRD analysis of fluoride precipitation at pH value of 4.5

4.6.7 Proximate analysis

The proximate analysis were done on the SPL samples as well as on the optimized samples of the samples obtained from the experiments. It was found that the carbon percentage increased upon subsequent treatment.

Table 4.13 Proximate analysis of SPL samples

Sample	Moisture content (%)	Residue content (%)	Volatile matter (%)	Fixed carbon (%)
Raw SPL	3.46	51.89	6.18	38.46
Water Washed SPL	2.40	51.32	5.91	40.37
Alkali treated SPL	2.20	25.25	4.78	67.77
Final treated SPL (NaOH fallowed by H_2SO_4)	2.13	16	3.19	78.68

4.6.8 Calorific value analysis:

The heat of combustion (calorific value) of raw SPL, water wash SPL, treated water wash SPL with 1.5 M NaOH, treated sample with 1.5 M NaOH followed by 2.5 M H_2SO_4 and treated sample with 1.5 M NaOH followed 2.5 M H_2SO_4 were done with Parr 6100 calorimeter. The results are tabulated in the table 4.14.

Table 4.14 Calorific value of raw SPL to treated SPL with H_2SO_4

Compounds	Calorific value (cal/g)
Raw SPL	2865.0418
Water wash SPL	3924.8990
Alkali treated SPL	5057.5625
Final treated SPL (NaOH fallowed by H_2SO_4)	6689.6948

CHAPTER 5

CONCLUSION

5. CONCLUSION

- When SPL containing Na_3AlF_6 was dissolved in excess sodium hydroxide, $Al(OH)_6^{3-}$ and $Al_2(OH)_{10}^{4-}$ was formed according to the reactions 4.3 and 4.4.
- Higher the F value more the predominating factor in the leaching percentage. From the F-test and ANOVA analysis, we have found the significant factors which play a vital role in the calculation of leaching percentage. In case of perchloric acid, temperature has been found out to be the most significant factor among all the parameters, whereas the L/S ratio is the most insignificant among the four parameters studied. Temperature contributed 77.7% in the leaching process, whereas L/S ratio contributed only 4.7 %. For sulfuric acid, alkali concentration has been the most significant factor among the four parameter studied. Alkali concentration contributed 44.96% whereas temperature contributed only 11.94%.
- In classical approach of optimization the maximum leaching percentage was found to be 54.12% for perchloric acid and 49.18% for sulfuric acid whereas in Taguchi optimization method the maximum leaching percentage was 51.24% for perchloric acid and 52.39% for sulfuric acid. This clearly indicates that Taguchi optimization method is fairly satisfactory in finding the maximum leaching percentage.
- The carbon percentage of SPL was found out to increase from 42.19% to 87.03% as confirmed from the ultimate analysis. From the proximate analysis, the fixed carbon was found to have been increased from 38.96% to 82.86 % for perchloric acid and 38.96% to 78.68% for sulfuric acid from the raw to final treated SPL which makes it possible to use it as a source of energy for power plants.
- From XRD analysis it is concluded that in case of perchloric acid at lower pH value of the solution favors higher degree of precipitation of cryolite is favoured and in case of sulfuric acid both the condition of pH were satisfied for the cryolite precipitation.
- From the calorific value determination it is seen that the heating value of raw SPL (2865.041 cal/g) has substantially increased to 6533.647 cal/g and 6689.694 cal/g respectively by using perchloric acid and sulfuric acid. It is therefore concluded that the treated SPL can be satisfactorily used as a substitute of raw coal as a fuel in the power plants, whose gross calorific value on an average varies within the range of 3800 cal/g to 4300 cal/g (for most indian coal).

5.1 Future recommendations:

Following recommendations are suggested for future research:

- Leaching process can be explored with different types of alkali-acid combination at different concentration, L/S ratio and temperature.
- Apart from the use of SPL as a possible fuel material, studies as other gainful utilization of SPL e.g. Recovery of carbon for electrode manufacture or other carbon articles can be undertaken in future.
- Any other possible methods of removal of fluoride and other harmful elements can be undertaken as a future study for safe disposal of SPL to the environment, which happens to be the serious problem for all aluminium industries worldwide.

CHAPTER 6

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6. REFERENCES

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